

Attorney Docket No. 2001.45

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:  
Jaime Navarrete

Art Unit: 1745

Serial No. 10/664,147

Examiner: T. M. Dove

Filed: September 17, 2003

For: THE USE OF GRASS LIGNINS IN THERMOPLASTICS

**APPEAL BRIEF**

Mail Stop Appeal Brief-Patents  
Commissioner for Patents  
P. O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

This Appeal Brief is filed simultaneously with the Notice of Appeal in reply to the Office Action mailed June 9, 2005.

The fees required under Sections 41.20(b) (1) and 41.20(b) (2) are paid pursuant to instructions on the accompanying Fee Transmittal Sheet which is provided in duplicate.

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### **I. REAL PARTY IN INTEREST**

Daramic, Inc., is the real party in interest as the assignee of record in the instant application.

### **II. RELATED APPEALS AND INTERFERENCES**

There are no related appeals or interferences.

### **III. STATUS OF THE CLAIMS**

Claims 1-14 were filed in this case. Claims 10-14 drawn to a thermoplastic polymer were restricted out of this case by the Examiner. In the Amendment of March 17, 2005, claim 8 was cancelled. Claims 1-7 and 9 stand finally rejected under 35 U.S.C. 102(b) as being anticipated from Navarrette. Applicant amended claims 4 and 9 in an amendment after final filed on July 25, 2005. The Examiner withdrew the 35 U.S.C. 112, second paragraph to claims 21-26, in the advisory action of August 4, 2005. The Examiner has indicated that the amendment after final would be entered for appeal purposes. Claims 1-7 and 9, finally rejected under 35 U.S.C. 102(b) are the subject of this Appeal.

#### **IV. STATUS OF AMENDMENTS**

Claims 4 and 9 were amended after the Final Rejection based on a rejection to claims 4 & 9 under 35 U.S.C. 112, second paragraph. In the Examiner's Advisory Action before the Filing of an Appeal, of August 4, 2005, the Examiner indicated that the amendment to claims 4 and 9 was entered for appeal purposes and that the rejection to claims 4 and 9 under 35 U.S.C. 112, second paragraph has been removed.

#### **V. SUMMARY OF THE CLAIMED SUBJECT MATTER**

The following is a concise explanation of the subject matter defined in independent Claims 1 and 6.

According to Claim 1, the instant invention is a battery separator (specification page 4, line 20) which comprises: a microporous membrane including, an ultra high molecular weight polyethylene (specification page 4, line 21), a filler (specification page 4, line 21), and a grass lignin (specification page 4, line 5).

According to Claim 6, the instant invention is a battery separator (specification page 4, line 20) which is comprised of a microporous membrane (specification

page 4, line 21) having an open cell structure (specification page 4, line 26) with pores sizes in the range of about 0.1 to about 1 micron (specification page 4, line 23) and porosity greater than 10% (specification page 4, line 23-24). The microporous membrane is comprised of about 15-25% by weight of an ultra high molecular weight polyethylene (specification page 5, line 2); about 50-80% by weight of a filler (specification page 5, line 2); and about 5-20% by weight of a grass lignin (specification page 5, line 3).

#### **GROUND'S OF REJECTION TO BE REVIEWED ON APPEAL**

Claims 1-7 and 9, stand finally rejected under 35 U.S.C. §102(b) as being anticipated from Navarrete are the subject of this Appeal.

#### **VI. ARGUMENT**

Claims 1-9 and 16-26, for the reasons explained hereinafter, are not anticipated from Navarrete under 35 U.S.C. §102(b), so the rejections must be removed.

§102(b) Rejections

Claims 1-7 and 9 stand rejected under 35 USC § 102(b) as being anticipated Navarrete et al. Applicant traverses.

The Examiner avers that Navarrete et al., WO 02/28955 A2 anticipates all the claims in the instant application under 35 USC § 102(b). It is the Examiner's opinion that the term grass lignin is a product by process claim which is incapable of distinguishing the Instant Application from Navarrete et al. which teaches the use of hardwood and softwood lignins. This is not true.

A compound or composition of matter is anticipated if the disclosure in a single reference places that compound or composition in possession of the public. See *In re Brown*, 329 F.2d 1006, 1011, 141 U.S.P.Q. 245, 249 (C.C.P.A. 1964). The reference must "clearly and unequivocally disclose the claimed compound or direct those skilled in the art to the compound without any need for picking, choosing, and combining various disclosures . . . . " *In re Arkley*, 455 F.2d 586, 587, 172 U.S.P.Q. 524, 526 (C.C.P.A. 1972). The reference must therefore provide a certain degree of precision with respect to the specific compound claimed.

As with *In re Brown*, the reference Navarrette clearly and unequivocally discloses a "compound or direct those skilled in the art to the compound without any need for picking, choosing, and combining various disclosures . . . . " On page 6, lines 12-13, of the WO reference, it is taught that "Lignins refers to those by-products of wood pulping operations". What the Examiner fails to mention is that the compound disclosed in Navarrette "wood lignins" are not the "grass lignins" of the Instant Invention. As in *In re Arkley*, The reference provides a certain degree of precision with respect to the specific compound claimed. Page 8, lines 16-17, of the WO reference teaches that "Lignins refers to those by-products of wood pulping operations". There is no mention or suggestion to use any other type of lignins.

For example, in *Ex parte Westphal*, 223 U.S.P.Q. 630 (Bd. Pat. App. 1983), the claim was directed to a composition containing 3-methylthio-4-amino-6-tert-butyl-1,2,4-triazine-5-one. The examiner rejected the claim under section 102 as anticipated by, *inter alia*, a patent to Fawzi. This patent disclosed a compound substituted at a particular position with alkyl having 1 to 8 carbon atoms, but did not specifically name the claimed tert-butyl radical. Thus, the board found that the Fawzi patent did not provide the precision necessary for anticipation under section 102. *Id.* at 631.

Similarly, in *Arkley*, the court found that the single claimed compound was not described in the prior art within the meaning of section 102. The prior art generically disclosed a class of compounds encompassing the claimed compound, as well as over 230,000 other compounds. The board contended, however, that the prior art contained two examples that disclosed the exact precursors of the claimed compound. The court found that these examples disclosed exact precursors only to the extent that one selects the correct acid to react with a particular tertiary amine, which also must be selected. See *Arkley*, 455 F.2d at 588, 172 U.S.P.Q. at 526. The court further found that there was nothing in the reference that "'clearly and unequivocally' directs those skilled in the art to make this selection . . . ." *Id.* Thus, the court reversed the rejection under section 102.

In the detailed description, Navarrete only discusses wood lignins as follows:

Lignin refers to those by-products of wood pulping operations having extremely complex chemical structures that consist primarily of phenyl propane linked together in three dimensions. Lignins include softwood lignins, hardwood lignins, and mixtures thereof. Hardwood lignins are preferred. Such lignins are commercially available from Westvaco Corp., Charleston, S.C. under the product name of PC-1369. (WO page 6, lines 12-20).

This same reference in the background of the invention discusses the differences between grass, softwood and



hardwood lignins on page 1, lines 15-26 and page 2,  
lines 1-2 as follows:

Lignin is a by-product of wood pulping operations. Lignin's chemical structure is extremely complex. Lignin is generally accepted to be a three dimensional, crosslinked polymer comprised of three different phenyl propenol moieties. The relative amounts of the three monomeric compounds, coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, vary with the sources of the lignin. Grass lignins, such as obtained from rice, corn, or sugar cane, are comprised predominantly of coumaryl and coniferyl alcohols. Softwood lignins, such as obtained from spruce, pine, redwood, cedar, and the like, are made up of predominantly coniferyl alcohol alone. Hardwood lignins are comprised of mostly coniferyl and sinapyl alcohols. Hardwood lignins are obtained, or substantially obtained, from oak, cherry, maple, birch, sweet gum, mahogany, and the like.

Therefore from the cited reference one of ordinary skill would reason that Grass lignins, are comprised predominantly of coumaryl and coniferyl alcohols. Softwood lignins, are made up of predominantly coniferyl alcohol alone and that hardwood lignins are comprised of mostly coniferyl and sinapyl alcohols. As the wood lignins fail to contain any significant amount of coumaryl alcohols no one of ordinary skill in the art would believe that these lignins from a chemical composition standpoint, would be interchangeable with the wood lignins.

The Examiner takes the position that the claim element "grass lignin" makes the claim a product-by-process claim, and thereafter, effectively, strikes the word "grass" from the claim to make the rejection. The Examiner gives no authority to back up this rejection. Applicant assumes, in that no authority is cited in the final rejection of June 6, 2005 by the Examiner, that the Examiner is relying upon In re Thorpe 227 USPQ 964, 966 (Fed Cir 1985) for this position which can be found in the MPEP 2113.

Applicant contends that the Examiner's position is incorrect and that instead the referenced claim element is a structural element.

First, Thorpe is misplaced. Thorpe's product-by-process claim was:

"44. The product of the process of Claim 1."  
and Thorpe's Claim 1 was a process claim. The Instant Claim 1 is cast in the product claim format. Claim 1 is:

"A battery separator comprising: a microporous membrane including, an ultra high molecular weight polyethylene, a filler, and a grass lignin."

The instant claim is not a "product-by-process" claim in the Thorpe sense. Instead, terms used in the claim are used as a noun. The term grass is not a process term. It is the Examiner's opinion that the source used to produce the lignin is considered a product-by-process limitation however no authority is given to support this conclusion. If one looks at the reference cited by the Examiner, it clearly defines some of the chemical differences between grass lignins and wood lignins on page 1, lines 15-26. If the referenced cited by the Examiner clearly explains how the lignins are different chemically it should be clear that the term grass (a noun and not a process term) is not a product by process limitation and is clearly differentiated from the prior art. Accordingly, Thorpe is misplaced in the instant situation.

Second, the clauses of the claim, "grass lignin," are structural terms. In re Steppan 156 USPQ 143, 148 (CCPA 1967), and In re Garnero 162 USPQ 221, 223 (CCPA 1969). In Steppan, the court viewed the "product-by-process" language, i.e. "condensation product," as a further qualifier of the invention. In the instant

claim, the questioned language further defines the lignin as a particular type of lignin, e.g. "grass" lignin as opposed to a "wood lignin". Both grass and wood lignins are recognized, in the art, as descriptors of different classes or types of lignins. See WO 02/28955 A2 (copy attached pages 21-35).

In Garnero, the court compared the "product-by-process" language, i.e. "interbonded," to a list of words that had previously been construed as structural terms. Appellant maintains that the questioned clause "grass" is modifiers of a noun "lignin" that structurally define that noun, just as the words reviewed in Garnero. Thus, the questioned clauses are structural elements of the claim and cannot be disregarded when considering patentability of the claims. Here the manufacturing process used to derive lignins from grass, as opposed to wood, impart distinctive structural characteristics to the final product. See the specification on page 4, lines 7-13:

The grass lignin acts as an antimony suppressor, which reduces antimony poisoning within the battery. When grass lignins are used, there is a less noticeable discoloration of the separator as in comparison to when wood lignins are used in battery separators. Furthermore, when grass lignins are used, the odor is dramatically

reduced as in comparison to when wood lignins are used in battery separators.

Even if the Examiner is correct in her assertion that "the source used to produce the lignin is considered a product-by-process limitation" there are abundant references in the literature, starting with the reference which is cited against patentability which state that the lignin produced from a grass source is structurally different from lignins from a wood source. The board is reminded here that the Examiner gives no authority to back up her accusation that there is no difference between grass and wood lignins. In the Evidence appendix attached are five different articles<sup>12345</sup> which teach that a lignin from a grass source is structurally different from a lignin derived from a wood source. As these articles are a fair representation of the knowledge of a person of ordinary skill in the art, they show that the rejection to the independent claims are improper and must be withdrawn.

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<sup>1</sup> Atmospheric Acetic Acid Pulping of Rice Straw IV

<sup>2</sup> Analytical protocols for characterization of sulphur-free lignin

<sup>3</sup> Chemical Modification, Properties, and Usage of Lignin

<sup>4</sup> Plant Polyphenols of Importance for Humus Formation

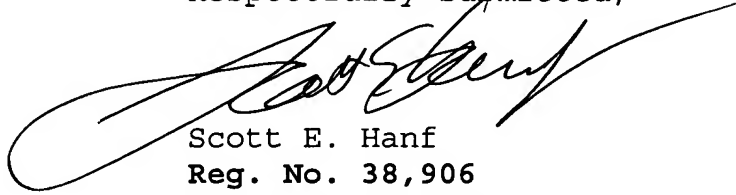
<sup>5</sup> Recent Industrial Applications of Lignin: A Sustainable Alternative to Nonrenewable Materials

### CONCLUSION

As stated above, the only question before the board is, if the feature of grass lignin of the instant invention differentiates the Instant Invention from the wood lignins clearly taught by Navarrete. It is the Examiner's position that grass lignin is a process limitation but the Examiner does not explain on what authority she uses to classify a non-process term such as grass as a process term. The reference, Navarrete, clearly sets forth some of the chemical differences between grass and wood lignins, if the reference used by the Examiner says that the chemical composition is different, how can she maintain that they are the same? In summary, the 35 USC § 102(b) reference the Examiner is citing against the Instant Application, Navarrete, teaches the use of "wood lignins" and set forth how "wood lignins" are chemically different from the Instant Applications "grass lignins" therefore it should be obvious from Navarrete alone that the Instant Invention is not anticipated.

In view of the foregoing, Applicants respectfully request  
an early Notice of Allowance in this application.

Respectfully submitted,



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Attachments: Claim appendix (3 pages) 16-18  
Evidence appendix (69 pages) 19-87

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**VII CLAIM APPENDIX**

1. (previously presented) A battery separator comprising:
  - a microporous membrane including
  - an ultra high molecular weight polyethylene,
  - a filler, and
  - a grass lignin.
2. (original) The separator of claim 1 wherein said grass lignin comprises about 5-20% by weight of said membrane.
3. (original) The separator of claim 2 wherein said grass lignin comprises about 5-10% by weight of said membrane.
4. (previously presented) The separator of claim 1 wherein said grass lignin source being selected from the group consisting of: bagasse, straw, abaca, sisal, flax, jute, hemp, and combinations thereof.
5. (original) A lead acid battery including the separator of claim 1.



6. (previously presented) A battery separator comprises:  
a microporous membrane having an open cell structure  
with pores sizes in the range of about 0.1 to about 1 micron  
and porosity greater than 10%, and where said microporous  
membrane comprises:

about 15-25% by weight of an ultra high molecular  
weight polyethylene;

about 50-80% by weight of a filler;

about 5-20% by weight of a grass lignin.

7. (original) The separator of claim 6 wherein said  
filler being selected from the group consisting of precipitated  
silica, oxide compounds, and mixtures thereof.

8. (cancelled) ~~The separator of claim 6 wherein said oil  
being selected from the group consisting of mineral oil,  
olefinic oil, parafinic oil, napthenic oil, aromatic oil, and  
mixtures thereof.~~

9. (previously presented) The separator of claim 6  
wherein said grass lignin source being selected from the group  
consisting of: bagasse, straw, abaca, sisal, flax, jute, hemp,  
and combinations thereof.

10. (withdrawn) A thermoplastic polymer formulation comprising:

up to about 80% by weight of the formulation being thermoplastic polymer;

up to about 20% by weight of the formulation being a processing oil, and

up to about 10% by weight of the formulation being a grass lignin.

11. (withdrawn) The formulation of claim 10 wherein said polymer being a polyolefin.

12. (withdrawn) The formulation of claim 10 wherein said polymer being an ultrahigh molecular weight polyethylene.

13. (withdrawn) The formulation of claim 10 wherein said polymer includes a filler.

14. (withdrawn) The separator of claim 10 wherein said grass lignin being sourced from bagasse, straw, abaca, sisal, flax, jute, hemp, and combinations thereof.

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ART UNIT 1745

**VIII Evidence Appendix**

Reference	Pages
1. Reference cited by Examiner WO 02/28955 A2	20-35
2. Atmospheric Acetic Acid Pulping of Rice Straw IV	36
3. Analytical protocols for characterisation of sulphur-free lignin	37-58
4. Chemical Modification, Properties, and Usage of Lignin	58-75
5. Plant Polyphenols of Importance for Humus Formation	76-85
6. Recent Industrial Applications of Lignin: A Sustainable Alternative to Nonrenewable Materials	86-87

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Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MY, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, HU, IT, LI, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

— as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MY, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, HU, IT, LI, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

— of inventorship (Rule 4.17(iv)) for US only

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: THE USE OF LIGNINS IN THERMOPLASTICS

(57) Abstract: The instant invention is directed to the use of lignin in thermoplastics (such as: ultra-high molecular weight polyethylene (UHMWPE)). In the first aspect of the invention, lignins are added to a lead acid battery separator comprising a microporous membrane including an ultra-high molecular weight polyethylene, a filler, and a processing oil. In the second aspect of the invention, lignins are used as a processing aid in thermoplastics.

WO 02/28955 A2

## THE USE OF LIGNINS IN THERMOPLASTICS

### Related Application

This application is a continuation-in-part of co-pending U.S. application Serial No. 09/677,435, filed October 3, 2000.

### Field of the Invention

This invention is directed to the use of lignins in thermoplastics (such as: ultra-high molecular weight polyethylene (UHMWPE)).

### Background of the Invention

Lignin is a by-product of wood pulping operations. Lignin's chemical structure is extremely complex. Lignin is generally accepted to be a three dimensional, crosslinked polymer comprised of three different phenyl propanol moieties. The relative amounts of the three monomeric compounds, coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, vary with the sources of the lignin. Grass lignins, such as obtained from rice, corn, or sugar cane, are comprised predominantly of coumaryl and coniferyl alcohols. Softwood lignins, such as obtained from spruce, pine, redwood, cedar, and the like, are made up of predominantly coniferyl alcohol alone. Hardwood lignins are comprised of mostly coniferyl and sinapyl alcohols. Hardwood lignins are

obtained, or substantially obtained, from oak, cherry, maple, birch, sweet gum, mahogany, and the like.

A thermoplastic refers to a polymer that softens or melts when exposed to heat and returns to its original condition when cooled. Ultra-high molecular weight polyethylene (UHMWPE) refers to a polymer with molecular weight greater than 1 million and preferably in the range of about 5 million to about 7 million. UHMWPE has many unique properties, but it is extremely difficult to process, i.e., form into usable shapes. Conventional extrusion and molding techniques can not be used. When extrusion techniques are used, the energy added to the polymer by the extruder may cause chain scissions (e.g., thermal degradation) which, in turn, detrimentally effects the polymer. Rubin, I.I., Editor, *Handbook of Plastic Materials and Technology*, John Wiley & Sons, Inc., NYC, NY, (1990), p. 349-354, Stein, H.L., "Ultra High Molecular Weight Polyethylene (UHMWPE)", *Engineered Materials Handbook, Vol. 2 Engineering Plastics*, ASM International, Metals Park, OH, 1988, and U.S. Patent No. 4,778,601, each is incorporated herein by reference. One method of extruding UHMWPE is to mix the UHMWPE resin with a mineral oil (or plasticizer), for example 80-98% by weight UHMWPE and 2-20% by weight mineral oil. The uniformly dispersed oil allows the UHMWPE to flow more easily through the extruder. See U.S. Patent No. 4,778,601.

In the first aspect of the invention, lignins are added to an ultra-high molecular weight polyethylene battery separator for a lead acid battery for, in part, reducing antimony poisoning.

Poisoning of lead acid storage batteries is known. One poison is antimony (Sb) which is an alloying component of the lead used in the batteries. Antimony poisoning causes a reduction in hydrogen overvoltage. Several solutions to the antimony poisoning problem have been suggested. For example, see: U.S. Patent 5,221,587 - an uncrosslinked natural or synthetic rubber is a layer on or incorporated into microporous or glass fiber separators (also see column 2, line 51 - column 3, line 14 for a discussion of additional solutions); U.S. Patent 5,759,716 - organic polymers having an affinity for the metal impurity (e.g., Sb) are incorporated into, for example, the separator; European Published Application No. EP 0 910 130 A1 - thioglignins are incorporated into fibrous separators; and Japanese Published Application (Kokai) No. 11-191405 - lignins are impregnated or coated on a glass mat separator.

In the second aspect of the invention, lignins are added to thermoplastic polymer formulations to act as a processing flow aid.

### Summary of the Invention

The instant invention is directed to the use of lignins in thermoplastics (such as: ultra-high molecular weight polyethylene (UHMWPE)). In the first aspect of the invention, lignins are added to a lead acid battery separator comprising a microporous membrane including an ultra-high molecular weight polyethylene, a filler, and a processing oil. In the second aspect of the invention, lignins are used as a processing aid in thermoplastics.

### Detailed Description of the Invention

In the first aspect of this invention, a lignin is added to a microporous battery separator for a lead acid battery made from ultra-high molecular weight polyethylene. The lignin acts as an antimony suppressor which reduces antimony poisoning within the battery. Battery separators made with ultra-high molecular weight polyethylene are known. See for example U.S. Patent 3,351,495; and Besenhard, J.O., Editor, *Handbook of Battery Materials*, Wiley-VCH, NYC, NY (1999) p. 258-263, both are incorporated herein by reference.

The lead acid battery separator generally comprises a microporous membrane made from UHMWPE, fillers, processing oil and lignin. The microporous membrane has an average pore size in the range of about 0.1 to about 1.0 micron, a porosity greater than 10% (preferably between about 55% and about 85%; and most



preferably between about 55% and about 70%), and the pore structure is referred to as an open cell structure or interconnected pore structure. The membrane generally comprises about 15-25% by weight UHMWPE, 50-80% by weight filler, 0-25% by weight process oil, and 5-20% lignin. Additionally, minor amounts of processing aids may be added. Preferably, the membrane comprises 17-23% by weight UHMWPE, 50-60% filler, 10-20% processing oil, and 5-10% lignin. These materials are mixed and extruded in a known fashion. See, for example: U.S. Patent No. 3,351,495; and Besenhard, J.O., Editor, *Handbook of Battery Materials*, Wiley-VCH, NYC, NY (1999) p. 258-263, both are incorporated herein by reference.

UHMWPE refers to polyethylenes with a molecular weight greater than 1 million, preferably greater than 3 million. UHMWPE are commercially available from Ticona LLC, Bayport, TX, and Montell, Inc., Wilmington, DE.

Filler refers to high surface area particles with an affinity for the processing oil. Preferred fillers include precipitated silica, oxide compounds, and mixtures thereof. Such silicas are commercially available from PPG, Pittsburgh, PA and Degussa-Huls AG, Frankfurt, Germany. Also see U.S. Patent Nos. 3,351,495 and 4,861,644, incorporated herein by reference, for additional filler suggestions.

Processing oil (or plasticizer) refers to, for example, mineral oil, olefinic oil, parafinic oil, naphthenic oil, aromatic oil, and mixtures thereof. Processing oil performs two functions; first, it improves the processability of UHMWPE, and second, it is the extractable component, which is used to create the microporous structure of separator. Mineral oil is preferred and is commercially available from Equilon of Houston, TX. Also see U.S. Patent Nos. 3,351,495 and 4,861,644, incorporated herein by reference, for additional processing oil (or plasticizer) suggestions.

Lignin refers to those by-products of wood pulping operations having extremely complex chemical structures that consist primarily of phenyl propane linked together in three dimensions. Lignins include softwood lignins, hardwood lignins, and mixtures thereof. Oak or maple flour may also be used, but because the lignins have not been separated from the cellulose fibers, they are more difficult to process. Hardwood lignins are preferred. Such lignins are commercially available from Westvaco Corp., Charleston, SC under the product name of PC-1369.

Further explanation of this aspect of the invention will be set out in the examples below.

In the second aspect of the instant invention, a lignin may be added to a thermoplastic polymer as a processing aid (e.g., flow lubricant).

In general, it has been found that when up to 10% by weight of the lignin is added to the thermoplastic polymer or the thermoplastic polymer formulation that beneficial results are obtained. Those results include decreased process temperature and polymer viscosity, and increased strength of end product. While not wishing to be bound by the following, it is believed that the lignin is able to reduce thermal degradation (chain scission) of the polymer during processing.

A thermoplastic polymer formulation preferably refers to a mixture of thermoplastic polymer, processing oil (or plasticizer), and lignin. In general, the formulation may be 60-80% thermoplastic polymer, up to 20% processing oil, and up to 10% lignin. Preferably, the formulation may be about 70-80% thermoplastic polymer, 15-20% processing oil, and 5-10% lignin.

A thermoplastic polymer refers to a polymer that softens or melts when exposed to heat and returns to its original condition when cooled. Natural substances that exhibit this behavior are crude rubber and a number of waxes; however, the term is usually applied to synthetics such as polyvinyl chloride, nylons, fluoropolymers, polyethylene (including ultrahigh molecular

weight polyethylene), polystyrene, polypropylene, acrylic resins, other macromolecules, and combinations thereof. Preferably, the thermoplastic polymer is a polyolefin. Most preferably, the thermoplastic polymer is ultrahigh molecular weight polyethylene (UHMWPE). The thermoplastic polymer may also be a mixture of the polymer and a filler. The filler is as discussed above. The ratio of filler to product is about 1.2:1 to about 5:1, preferably about 2.8:1.

Processing oil (or plasticizer) refers to, for example, mineral oil, olefinic oil, paraffinic oil, naphthenic oil, aromatic oil, and mixtures thereof. Also see U.S. Patent Nos. 3,351,495 and 4,861,644, incorporated herein by reference, for additional processing oil (or plasticizer) suggestions.

Lignin refers to those by-products of wood pulping operations having extremely complex chemical structures that consist primarily of phenyl propane linked together in three dimensions. Lignins include softwood lignins, hardwood lignins, and mixtures thereof. Hardwood lignins are preferred. Such lignins are commercially available from Westvaco Corp., Charleston, SC under the product name of PC-1369.

Further explanation of this aspect of the invention will be set out in the examples below.

Examples

The formulations set out in Table 1 were prepared.

**TABLE 1**  
(% By Weight)

Sample	Polymer (UDMAPE)	Filler (Silica)	Oil (Mineral Oil)	Minor Ingredients	Lignin
1	22.1	57.9	17.2	2.8	0
2	22.0	57.1	17.1	2.8	1 (Hardwood)
3	20.9	54.3	17.0	2.8	5 (Hardwood)
4	20.3	52.9	17.0	2.8	7 (Hardwood)
5	20.2	52.5	17.0	2.0	7.5 (Hardwood)
6	19.5	50.6	17.0	2.9	10.0 (Hardwood)
7	20.2	52.5	17.0	2.8	7.5 (Softwood)
8	19.5	50.6	17.0	2.9	10.0 (Softwood)
9	16.9	43.3	17.0	2.8	20.0 (Softwood)
10	20.9	54.3	17.0	2.8	5.0 (Oakwood flour)
11	19.5	50.6	17.0	2.9	10.0 (Oakwood flour)
12	20.9	54.3	17.0	2.8	5.0 (Maplewood flour)
13	20.2	52.5	17.0	2.8	7.5 (Maplewood flour)
14	19.5	50.6	17.0	2.9	10.0 (Maplewood flour)
15	16.9	43.3	17.0	2.8	20.0 (Maplewood flour)

The formulations of Table 1 set out in Table 2 were tested for Sb suppression. Results below were obtained via a cyclic voltammetry technique. Cyclic voltammetry techniques are known. Dietz, H., et al, "Influence of substituted benzaldehydes and their derivatives as inhibitors for hydrogen evolution in lead/acid batteries," 53 Journal of Power Sources 359-365 (1995), incorporated herein by reference.

TABLE 2

Sample	Sb Peak Height (mA)	Current (mA) at start of sweep @ -1.100 V
Control (15ppm Sb)	2.8	1.9
3	0.1	0.0
5	0.0	0.1
6	0.1	0.0
7	0.1	0.1
8	0.1	0.1
9	0.1	0.1
10	0.3	0.1
11	0.1	0.0
12	0.0	0.1
13	0.0	0.1
14	0.0	0.1
15	0.0	0.1

The formulations of Table 1 set out in Table 3 were tested for viscosity reduction. Formulations were tested using Kayeness Rheometer Galaxy III Model 9052, available from Kayeness, Inc. of Morgantown, PA.

TABLE 3

Sample	1	2	3	4
Shear rate (1/sec)	Shear Viscosity (Pa-sec)			
1368	1.94E+02	1.76E+02	1.58E+02	1.54E+02
547	4.32E+02	3.93E+02	3.52E+02	3.41E+02
164	1.01E+03	8.97E+02	8.68E+02	8.44E+02
55	2.01E+03	1.96E+03	1.92E+03	1.80E+02
16	4.83E+03	4.51E+03	4.77E+03	4.59E+03
6	1.23E+04	1.19E+04	1.19E+04	1.14E+03
2	2.27E+04	2.21E+04	1.93E+04	2.30E+04
1	9.88E+04	8.57E+04	8.32E+04	9.40E+04

The present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof and, accordingly, reference should be made to the appended claims, rather than the foregoing specification, indicating the scope of the invention.

## In the Claims:

1. A battery separator for lead acid batteries comprising:  
a microporous membrane including  
an ultra high molecular weight polyethylene,  
a filler,  
a processing oil, and  
a lignin.
2. The separator of claim 1 wherein said lignins being  
selected from the group consisting of softwood lignins, hardwood  
lignins, and mixtures thereof.
3. The separator of claim 1 wherein lignin comprises about  
5-20% by weight of said membrane.
4. The separator of claim 1 wherein said lignin comprises  
hardwood lignin.
5. The separator of claim 1 wherein said lignin comprises  
about 5-10% by weight of said membrane.
6. A lead acid battery including the separator of claim 1.



7. A battery separator for a lead acid battery comprises:  
a microporous membrane having an open cell structure  
with pores sizes in the range of about 0.1 to about 1 micron and  
porosity greater than 10%, and further comprising  
about 15-25% by weight of said separator being an ultra  
high molecular weight polyethylene;  
about 50-80% by weight of said separator being a  
filler;  
less than about 25% by weight of the separator being a  
processing oil;  
about 5-20% by weight of the separator being a lignin.
8. The separator of claim 7 wherein said filler being  
selected from the group consisting of precipitated silica, oxide  
compounds, and mixtures thereof.
9. The separator of claim 7 wherein said oil being  
selected from the group consisting of mineral oil, olefinic oil,  
parafinic oil, napthenic oil, aromatic oil, and mixtures thereof.
10. A thermoplastic polymer formulation comprising:  
up to about 80% by weight of the formulation being  
thermoplastic polymer;  
up to about 20% by weight of the formulation being a  
processing oil, and

up to about 10% by weight of the formulation being a lignin.

11. The formulation of claim 10 wherein said lignin being a hardwood lignin.

12. The formulation of claim 10 wherein said polymer being a polyolefin.

13. The formulation of claim 10 wherein said polymer being an ultrahigh molecular weight polyethylene.

14. The formulation of claim 10 wherein said polymer includes a filler.

15. A method for improving the processing of thermoplastic polymer comprising the step of:

adding a lignin to a thermoplastic polymer prior to the processing.

16. The method according to claim 15 wherein up to 10% by weight of said lignin being added.

17. The method according to claim 15 wherein the lignin being added to a blend of polymer and processing oil.

18. The method according to claim 15 wherein the polymer being a polyolefin.

19. The method according to claim 15 wherein the polymer being an ultrahigh molecular weight polyethylene.

20. The method according to claim 15 wherein the lignin being a hardwood lignin.

# Atmospheric Acetic Acid Pulping of Rice Straw IV: Physico-Chemical Characterization of Acetic Acid Lignins from Rice Straw and Woods. Part 1. Physical Characteristics

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Lignins obtained by atmospheric acetic acid delignification of rice straw, birch and fir were characterized by molecular weight, solubility and thermomechanical analysis, and by ultraviolet (UV), Fourier transform infra-red (FTIR) and  $^{13}\text{C}$ -NMR spectroscopy. Rice straw lignins (rice lignins) were very different from birch and fir lignins. The former was difficult to dissolve in most tested solvents and infusible on heating, while the latter had a good solubility and fusibility. FTIR spectra indicated that the rice lignins had more conjugated and fewer unconjugated carbonyl groups than the wood lignins.  $^{13}\text{C}$ -NMR spectra showed that rice lignins had more polysaccharides associated to the lignin and more *p*-coumaric and ferulic acid than the wood lignins. Concentrations of acetic acid and choice of catalyst (sulfuric or hydrochloric acid) had a considerable effect on the characteristics of rice lignins. Rice lignin obtained with 90% acetic acid than that obtained with 80% acetic acid, and the lignin obtained with sulfuric acid as catalyst than that obtained with hydrochloric acid, had lower molecular weight, better solubility, lower glass-transition temperature and lower UV absorptivity. 80% acetic acid delignified rice straw less effectively than 90% acetic acid.

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## Analytical protocols for characterisation of sulphur-free lignin

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### Abstract

Round robin tests for chemical characterisation of sulphur-free lignins, precipitated from black liquors of alkaline pulping of annual fibre crops, flax, hemp and straw, have been performed to identify quality-related properties. The total (Klason and acid soluble) lignin contents of these lignins range between 83 and 97%. Contaminants may be present, like sugar residues (< 3.2%), ash (< 5.2%), including Si (< 0.9%), and relatively high amounts of nitrogen (< 1.6%). Furthermore, the (oxidised) acid precipitated soda lignins were found to contain significantly less phenolic hydroxyl and more carboxyl groups than organosolv lignin (Alcell<sup>TM</sup>).

A comparison of FTIR and wet chemical methods indicated that acetylation for determination of hydroxyl groups under the conditions used is incomplete, resulting in an unreliable total hydroxyl determination. Molecular weight analysis of the round robin lignins using HPSEC with different eluents gave incomparable results. Number average molecular weights of the lignins, as found by VPO, are relatively low. Compared to Alcell<sup>TM</sup> lignin, soda lignins from flax, hemp and straw have different compositions, functional groups and molecular weights, which confirms that different functional properties are related to the chemical structure.

Protocols have been established for reproducible determination of the chemical composition, functional groups, such as phenolic hydroxyl and carboxyl groups and number average molecular weight of alkaline lignins from annual fibre sources.

**Keywords:** Non-wood lignin characterisation; Sulphur-free lignin; Soda lignin; Round robin; Functional groups; Molecular weight; Annual fibre crops; Alcell<sup>TM</sup> lignin

### 1. Introduction

Together with cellulose, lignin belongs to the most abundantly occurring renewable resources. Almost all lignin extracted from lignocellulosic materials for paper production in modern pulp mills is burned to generate energy and recover chemicals. The lack of other, value added, applications is mainly caused by the heterogeneity, odour and colour problems of lignin based products. Moreover, the absence of well-defined, standard analytical protocols, adopted by both suppliers and end-users of lignins in different markets is an important issue (Glasser, 2000) for its broader introduction as raw material in industry.

The heterogeneity of lignin is caused by variations in the polymer composition, size, cross linking and functional groups. Differences exist in molecular composition and linkage type between the phenylpropane monomers, p-hydroxyphenyl, guaiacyl and syringyl units, derived from respectively coumaryl, coniferyl and sinapyl alcohol precursors. Lignin composition will be different not only between plants of different genetic origin, but also between different tissues of an individual plant. In softwood lignin, the structural elements are predominantly derived, for more than 95%, from coniferyl alcohol. In hardwoods (and dicotyl crops like flax and hemp) various ratios of coniferyl/sinapyl have

also result  
Conclusions



been observed, whereas in lignin derived from cereal straws and grasses the presence of coumaryl alcohol is typical (Dence and Lin, 1992). The major chemical functional groups in lignin include hydroxyl, methoxyl, carbonyl and carboxyl groups in various amounts and proportions, depending on genetic origin and applied extraction processes.

Recently, the interest in using non-wood fibres for the production of cellulose for paper and other industrial applications is growing (De Jong *et al.*, 1999, Molita *et al.*, 2000). Extracted lignins from non-wood fibres are potential raw materials for new industrial applications. Sulphur-free lignin, as a renewable raw material, is of increasing interest, because of ecological and economical aspects. Lignin derived from non-wood fibres is commercially available through a Swiss company that patented a precipitation method for lignin isolation from black liquors (Abächerli and Doppenberg, 1998). Separation of lignin from alkaline waste water of cellulose production is achieved by acidification and filtration. In the alkaline pulping process no sulphur-containing chemicals are used, so sulphur-free alkaline lignin is obtained. Application development for this type of lignin is studied in a research project (FAIR CT 98-3521) funded by the European Commission with participation of several producers of black liquor from non-wood alkaline pulping, research institutes and industrial companies, which are active on markets including (bio)polymers, polymer additives, wood adhesives and surfactants.

Lignins studied in this programme are derived from alkaline pulping of annual (fibre) crops, such as wheat straw, hemp and flax. For enhanced utilisation of lignin, reliable characterisation methods should become available for identification of chemical and physical properties. Due to the structural complexity of lignin, development of reproducible methods is rather difficult, as described by several researchers (Milne *et al.*, 1992, Lin and Dence, 1992). To obtain reliable protocols yielding exchangeable results, a round robin for the characterisation of alkaline lignins from annual fibres was performed by five laboratories. The characterisation methods comprise determination of solubility in different solvents, chemical composition, functional groups, such as phenolic and aliphatic hydroxyl, carboxyl groups and molecular weight. Participating laboratories used both their own methodology and the proposed procedures by the other partners. Several methods used were derived from existing protocols (Lin and Dence, 1992).

The goals of the round robin are the reliable determination of the functional properties of lignins and the establishment of analytical protocols for characterisation. Alcell<sup>™</sup> organosolv lignin was used as a reference lignin, because this lignin has been extensively characterized previously by several researchers in a round robin (Milne *et al.*, 1992).

## 2. Material and Methods

### 2.1. Lignins

Lignins from alkaline pulping of wheat straw, hemp and flax were obtained after precipitation by acidifying black liquor from Spanish pulp mills and subsequent purification according to a patented process (Abächerli and Doppenberg, 1998). Two flax lignins were derived from the same black liquor, but the lignins were recovered at different precipitation pH of respectively 5.5, for flax1 lignin, and 2, for flax2 lignin.

Alcell<sup>™</sup> organosolv lignin was obtained from Dr. Jairo H. Lora from Repap Technologies Inc., Valley Forge, PA, USA. This lignin was extracted from mixed hardwoods (maple, birch and poplar) by an organosolv process using aqueous ethanol.

### 2.2. Analytical methods

As reference compounds, syringic acid and Alcell<sup>™</sup> organosolv lignin were used. Chemicals of analytical grade were used.

#### Structural characterisation of lignins by FTIR

Finely powdered lignin was pressed on the diamond surface of an ATR probe (Golden Gate ATR probe, Specac, United Kingdom). 16 scans were recorded on a Vector 33 infrared spectrometer (Bruker, Germany).

#### Carboxylic groups: "acid number" determination

The pH of 100 ml 95% (v/v) ethanol in water was adjusted to 9.0 using 0.1 mol l<sup>-1</sup> sodium hydroxide in water. After adding 1 g accurately weighed air dry lignin, of known dry weight, the

mixture was stirred for 10 min and subsequently titrated back to pH 9.0 with  $0.1 \text{ mol l}^{-1}$  sodium hydroxide in water.

#### Carboxylic groups: aqueous titration

Accurately weighed 1 g lignin was suspended in 10 ml alkaline aqueous solution. After 1 hour of stirring, the pH was adjusted to 12 with sodium hydroxide. After another 2 hours stirring, the solution was potentiometrically titrated with  $0.1 \text{ mol l}^{-1}$  aqueous hydrochloric acid.

#### Phenolic hydroxyl and carboxylic groups : non-aqueous titration

The phenolic hydroxyl and carboxylic groups were determined by a non-aqueous potentiometric titration with tetra-n-butylammonium hydroxide (TnBAH) (Dence, 1992). 0.15 g Lignin on dry weight basis and 0.02 g p-hydroxybenzoic acid as internal standard were used and the dissolving time of the lignins in DMF was extended to 15 minutes.

#### Phenolic hydroxyl groups: infrared spectroscopy

Determination of phenolic hydroxyl groups of lignin was performed using FTIR by determination of the aliphatic and aromatic ester bands of acetylated lignin at respectively  $1745$  and  $1765 \text{ cm}^{-1}$  and using a found equation (Wegener and Strobel, 1992). A Genesis Series FTIR Spectrometer of Analytical Technology Inc. (ATI Mattson, USA) equipped with a single reflection diamond attenuated total reflection probe was used.

#### Phenolic hydroxyl: non-aqueous titration with potassium methylate

Lignin was washed with DMF and dried before titration. 25% or 50% (w/w) lignin solution in DMF was potentiometrically titrated with  $0.1 \text{ N}$  potassium methylate.

#### Total hydroxyl groups

Acetylation of 1 g air dry lignin, of known dry weight, was performed by reaction in 20 ml pyridine : acetic anhydride mixture (1:1 v/v). After stirring for 24 hours under nitrogen at room temperature, 25 ml ice-cooled 100% methanol was added. The product was evaporated at reduced pressure to dryness and suspended in toluene and again evaporated to dryness. This was repeated three times. After this, methanol was added and the residue was again evaporated to dryness (Gellerstedt, 1992). The quantitative content of hydroxyl groups in lignin was determined by saponification of the acetyl groups and subsequent analysis by HPLC (Gosselink *et al.*, 1995).

Two types of lignin, straw and Alcell<sup>™</sup> lignin, were subjected to a second analytical method: 0.5 – 0.8 g air dry lignin of known dry weight was added to 10.00 ml acetic anhydride : pyridine 1 : 4 (v/v) and the obtained mixture was heated for 1 hour in an oil bath at  $90^\circ \text{C}$ . After adding 2 ml water and 5 minutes stirring, 50 ml ethanol was added to the mixture. Subsequently, the acetylated lignin was potentiometrically titrated with  $0.1 \text{ mol l}^{-1}$  sodium hydroxide in ethanol.

#### Ratio phenolic : aliphatic hydroxyl content

Aliphatic hydroxyl content of lignin was calculated from the difference of phenolic and total hydroxyl content as determined by wet chemical protocols described above. For  $^1\text{H}$  NMR analysis, lignin was acetylated (Gellerstedt, 1992) and 20 mg was dissolved in 0.8 ml  $\text{CDCl}_3$ . Measurements were performed with a Bruker DPX-300 MHz NMR spectrometer. The ratio was determined by integrating the signals of the aromatic and aliphatic acetoxy groups at respectively 2.3 and 2.0 ppm.

$^{13}\text{C}$  NMR spectroscopy was performed on acetylated lignin dissolved in  $\text{DMSO}-d_6$  at a Bruker AC200 NMR spectrometer. To quantify the signals, the inverse gated decoupling technique was applied. A delay of 12 s between the acquisition of each scan combined with a 90 degree pulse was chosen. Quantification of the ester signals of the aliphatic (169 – 171 ppm) and aromatic hydroxyl groups (166.5 – 169 ppm) gave the ratio of phenolic : aliphatic hydroxyl groups (Robert and Brünow, 1984; Landucci, 1985).

FTIR spectra were recorded of acetylated lignin with a Genesis Series FTIR Spectrometer of Analytical Technology Inc. (ATI Mattson, USA). For determination of the ratio of the aliphatic and phenolic hydroxyl groups in lignin, the intensity of the ester bands at respectively  $1745$  and  $1765 \text{ cm}^{-1}$  were used (Faix *et al.*, 1994).



#### Lignin solubility

A total of 2 g air dry lignin, of known dry weight, was dissolved in 100 ml DMF with 0.2 mol l<sup>-1</sup> LiCl or THF overnight at room temperature. After filtration under reduced pressure, the residue was dried at 70 °C till constant weight.

#### Molecular weight distribution by HPSEC

Lignin was dissolved in DMF with addition of 0.2 mol l<sup>-1</sup> LiCl at room temperature at a concentration of 0.1 % (w/w) by gently shaking the solution for 1-2 minutes every 8-12 hours. After 24 hours, the lignin solution was injected on the size exclusion columns. Different columns and chromatographic conditions were used: One system consisted of a Cosmosil HPLC Si-gel SSL, low porosity column (Waters/Nacalai Tesque, Japan) connected with a Tessek SGX-1000 unmodified silica based column, 10 µm particles, medium porosity (Tessek Praha, Czech Republic). Size exclusion was performed at room temperature with DMF and 0.2 mol l<sup>-1</sup> LiCl, a flow rate of 0.3 ml l<sup>-1</sup> and UV detection at 280 nm.

A second system consisted of three styragel HR columns, HR0.5, HR2 and HR4, 7.8 mm I.D. x 300 mm, 5 µm particles and a precolumn (Waters, Effen-Leur, The Netherlands). Size exclusion was performed at 80 °C with DMF and 0.2 mol l<sup>-1</sup> LiCl, a flow rate of 1 ml/min and UV detection at 280 nm.

The third HPSEC system consisted of four PLgel columns of 50, 500, 1000 and 10000 Å (Polymer Laboratories Ltd., Birmingham, England). Size exclusion was performed at 30 °C with stabilised THF, a flow rate of 1 ml l<sup>-1</sup> and combined RI and UV 254 nm detection. The lignin concentration was 1 % (w/w) in THF.

System calibrations were performed with polystyrene standards ranging from 162 Daltons to 1200 kDaltons.

#### Molecular weight by Vapor Pressure Osmometry

The vapor pressure of lignin solutions ranging from 10 to 40 mg lignin in 1.5 ml DMF was measured after equilibration of the system (Osmometers Knaauer K7000) at 90 °C for 12 min. Calibration of the VPO (vapor pressure osmometry) system was performed with glucose pentaacetate under identical conditions.

#### Chemical composition

375 mg lignin was hydrolysed with 3.75 ml ice-cooled 12 mol l<sup>-1</sup> sulphuric acid during 1 hour at 30 °C. After dilution with 36.25 ml demineralised water and 5 ml solution of inositol in demineralised water at 5 g l<sup>-1</sup> (internal standard), hydrolysis was performed during 3 hours in boiling water. After cooling in ice-water, the hydrolysate was centrifuged for 15 min at 4000 r.p.m. Acid insoluble lignin was determined after filtration and hot water washing over a G4 glass filter crucible (TAPPI T249 cm-85, 1999, TAPPI T222 cm-83, 1999). Acid soluble lignin was spectrophotometrically determined at 205 nm (TAPPI UM250 cm-83, 1991). Sugar residues were determined as their corresponding alditol acetates after subsequent reduction and acetylation (TAPPI T249 cm-85, 1999) using gas liquid chromatography with a flame ionization detector on a CP-Sil 88 capillary column (Chrompack, Middelburg, The Netherlands). Uronic acids in the sulphuric acid hydrolysate were spectrophotometrically determined at a wavelength of 520 nm (Blumenkrantz and Asboe-Hansen, 1973).

Nitrogen content of approximately 80 mg air dried lignin of known dry weight was determined by a rapid N system (Nitrogen/protein analyser, Elementar Analysensysteme GmbH, Hanau, Germany). Combustion of lignin was performed at 960 °C. Nitrogen formed was quantitatively analysed by conductivity measurement.

The ash content of lignin was gravimetrically determined after incineration at 700 °C for 8 – 12 hours till black carbon particles have been disappeared. To the ash, 20 ml of 65% (w/w) nitric acid was added and boiled gently till a residual volume of 8 ml and subsequently 4 ml of concentrated sulphuric acid was added. This was heated till white fumes were evolved. 4 ml 65% (w/w) nitric acid was added in order to clarify the solution. If necessary, this addition was repeated. After cooling to room temperature, 50 ml demineralised water was added and boiled for some minutes. After filtration, the residue was washed, dried and weighed (TAPPI T245, 1994, Gurkan *et al.*, 1990).

### 3. Results and Discussion

#### 3.1. Structural characterisation

FTIR spectra show clear differences between the five lignins studied (figure 1). Between 3000 – 2800  $\text{cm}^{-1}$  C-H stretch in methyl and methylene groups are present in different quantities. In the flax lignins substantially higher quantities are present. The lignins contain carboxyl groups represented by carboxyl vibrations between 1750 – 1550  $\text{cm}^{-1}$ . Spectra of flax, hemp and straw lignin show three peaks, whereas the peak at 1647  $\text{cm}^{-1}$  seems to be absent in Alcell<sup>TM</sup> lignin. Water in lignin gives rise to a signal at 1625  $\text{cm}^{-1}$  and may interfere with the conjugated C=O band. At 1600 and 1510  $\text{cm}^{-1}$  aromatic skeletal vibration bands can be seen for all lignins. Between 1300 and 1000  $\text{cm}^{-1}$  very different bands and peak ratios are present due to various vibrations like C-O, C-H and C=O (Faix 1992). FTIR show that the lignins studied are distinctively structurally different, which will be further elaborated by the detailed analyses described in this paper.

#### 3.2. Chemical composition

Table 1 shows that analytical results obtained for Alcell<sup>TM</sup> lignin with respect to lignin, sugar and nitrogen contents are in very good agreement with the data of Milne *et al.* (1992). This indicates that the methods used can be considered being reliable and reproducible. Alcell<sup>TM</sup> lignin has a higher purity than most of the alkaline lignins studied, derived from annual fibre pulping. The lignin content of the samples studied is between 83 and 90%, with maximal 3.2% sugar-residues and 1.6% nitrogen content. Obviously, considerable amounts of protein seem to be present in the soda lignins. Up to 10% is calculated when using an average conversion factor for nitrogen to protein of 6.25. It is likely that strong linkages are present between proteins and precipitated lignins, which are resistant to the used extraction procedures. This is also found by Pan and Sano (2000) for alkaline lignins of wheat straw, which contain strongly associated protein, which was difficult to remove by liquid-liquid extraction.

The sugar composition in different lignins is depending on the genetic origin of the starting material as shown in table 1. The relative high retention of galactose in hemp is remarkable, indicating strong association of galactan with lignin. In straw lignin xylan seems to be most strongly associated to phenolic residues. The ash and silicate contents of the different soda lignins are - as expected for annual fibre crops - at a higher level than in wood lignin. However, the ash content of straw lignin is remarkably low since wheat straw is known for its relatively high silica contents. Although both flax lignins are derived from the same black liquor, table 1 shows that their compositions differ significantly. This is caused by different precipitation procedures for the lignin recovery at varying pH from 5.5, for flax1, to 2, for flax2 lignin.

Table 1. Chemical composition of round robin lignins

#### 3.3. Functional groups: phenolic hydroxyl and carboxylic groups

Quantitative determination of the phenolic hydroxyl groups in lignin by non-aqueous titration (in DMF) with tetra-*n*-butylammonium hydroxide (TnBAH) is inter-laboratory reproducible (figure 2). Titration (in DMF) with potassium methylate gives comparable results with the TnBAH titration (figure 3). Method validation by using syringic acid as a model compound proves its reliability. Interference of other weak acidic components, such as end-group amino acids of proteins, present in the sulphur-free lignins is assumed to be low. Obviously, the content of phenolic hydroxyl groups in Alcell<sup>TM</sup> lignin is almost double the amount of alkaline lignins from annual plants.

For the lignins examined, the non-aqueous titrations for determination of phenolic hydroxyl groups give poor correspondence with the FTIR data (figure 3). However, with the exception of the flax2 lignin, the same tendency for FTIR is found to overestimate the values obtained by non-aqueous titration. For some lignins the inflection point for the phenolic hydroxyl groups is hard to observe, which means that the standard deviation in the results increases to more than 10%.

Furthermore, acetylated lignin samples have been used for quantification of the phenolic hydroxyl groups by FTIR. Acetylation of syringic acid results in a poor conversion (73% w/w) of the total amount of phenolic hydroxyl groups, which may be attributed to sterical hindrance by two methoxyl groups (figure 4). Also for lignins the acetylation could be incomplete, which will affect the reliability of the method and underestimates the phenolic content. In the FTIR spectra of lignin the O-H stretch vibration signal at the 3410-3460  $\text{cm}^{-1}$  is strongly reduced after acetylation, but not completely absent in the FTIR spectra, which indicates incomplete reaction for the lignins studied. Based on the results

obtained, the methods are not fully comparable and the non-aqueous titrations are assumed to be most accurate.

- Fig. 2. Phenolic hydroxyl content of different lignins determined by different laboratories with non-aqueous TnBAH titration  
 Fig. 3. Comparison of phenolic hydroxyl content of lignins determined by different methods  
 Fig. 4. Determination of total hydroxyl content of lignin after different acetylation procedures

Determination of the total hydroxyl content of the round robin lignins was performed by two different acetylation procedures. Between both methods significant differences for straw and Alcell<sup>TM</sup> lignin are demonstrated (figure 4). As indicated above, the acetylation reaction could be incomplete resulting in an underestimation of the total hydroxyl content.

The ratio of phenolic and aliphatic hydroxyl groups of lignin determined by wet chemical and several spectroscopic methods shows poor correlation (figure 5). In FTIR and NMR analysis overlapping signals may easily introduce significant errors. Corresponding results are obtained for straw lignin, but more discrepancy is found between the data for the other lignins. Similar differences for absolute values obtained by wet chemical and spectroscopic methods were found by Faix et al. (1994). Obviously, the ratio of phenolic/aliphatic hydroxyl is higher for Alcell<sup>TM</sup> lignin than for the other lignins. The contribution of sugar contaminants to the total aliphatic hydroxyl groups can be neglected for Alcell<sup>TM</sup> lignin, but in case of the alkaline lignins a substantial contribution has to be accounted for (maximum 0.6 mmol g<sup>-1</sup>). After subtraction of the latter contribution of sugar contaminants, the ratio of phenolic/aliphatic hydroxyl of the alkaline lignins will increase to values which are still lower than for Alcell<sup>TM</sup> lignin.

- Fig. 5. Comparison of the ratio of phenolic/aliphatic hydroxyl groups of lignin determined by various analytical methods

Carboxylic acid group analysis in lignin by non-aqueous titration using TnBAH (figure 6) gives comparable inter-laboratory results. Method validation with syringic acid, which contains 5.05 mmol g<sup>-1</sup> carboxylic groups, demonstrates that this method is reliable and reproducible. The carboxyl contents of alkaline lignins from straw, hemp and flax are higher than has been found for organosolv lignin (Alcell<sup>TM</sup>).

- Fig. 6. Carboxyl content of lignin as determined with a non-aqueous TnBAH titration by different laboratories

The "acid number" method, using aqueous 95% ethanol as solvent, for the determination of carboxylic groups, gives good inter-laboratory reproducible results (figure 7). However, the carboxylic content of the round robin lignins show some variance for the three different titration methods (figure 8). For all methods used, the model compound, syringic acid, gives comparable and reliable results. The main reason for the variances is ascribed to the lignin solubility in the selected solvents. For the TnBAH titration DMF was used as solvent in which the solubility of the lignins examined is much higher than in the other solvents used (table 2). The accessibility of the carboxylic groups will be higher when using DMF as solvent, so the non-aqueous titration with TnBAH will probably give the most reliable results.

- Fig. 7. Carboxyl content of lignins determined with the "acid number" analysis by different laboratories  
 Fig. 8. Carboxyl content of lignins determined with different analytical protocols  
 Table 2. Solubility (%) of a 2% (w/w) lignin solution

### 3.4. Molecular weight

Primarily, the solubility of the round robin lignins in DMF with 0.2 mol l<sup>-1</sup> LiCl and in THF has been determined as is shown in table 2. Only the Alcell<sup>TM</sup> lignin is completely soluble in both solvents. Because the solubility of the alkaline lignins is very poor in THF, the results of the molecular weight determination in this solvent reflect only the dissolved lignin part, which is likely to be only the low molecular fraction. The weight average molecular weight ( $M_w$ ) of hardwood (Alcell<sup>TM</sup>) lignin is in the same range for the different solvents used (figure 9), but is considerably lower in THF, probably due to lower swelling and smaller hydrodynamic volume of the dissolved molecules and partially adsorption

on the stationary column phase. The other lignins studied give even higher deviations in the  $M_n$  as determined by SEC (figures 9 and 10).

For SEC two major problems have been encountered. Firstly, some of the lignins do not completely dissolve in the solvent. Secondly, adsorption of lignin molecules on the stationary phase of the columns used may occur, as seen by an increase of the baseline detection signal at the end of a sample run as compared to the initial signal (figure 11). The two HPSEC systems using DMF with  $0.2 \text{ mol l}^{-1} \text{ LiCl}$  give no reproducible results probably due to the different operational conditions and columns used. In conclusion, HPSEC of lignin in organic solvents gives poorly comparable inter-laboratory results for the round robin lignins examined. The same was found previously by Milne *et al.* (1992) for molecular weight analysis of different lignins under identical standard conditions.

Number average molecular weight ( $M_n$ ) of the lignins as determined by VPO using DMF as solvent indicates that flax and hemp lignin have molecular weights of approximately 600 Daltons comparable with the Alcell<sup>TM</sup> lignin. In contrast, the straw lignin has a higher molecular weight ( $M_n$ ) of about 1400 Daltons (figure 9). For VPO analysis it is known that the determination of  $M_n$  strongly depends on the presence of low molecular weight fractions in the lignin (Pla, 1992). For this reason the  $M_n$  found for the alkaline lignins are considered to be rather low. Alcell<sup>TM</sup> lignin has a  $M_n$  and  $M_w$  of respectively 800 and 1600 Daltons, when using THF as solvent, as found by Hergert *et al.* (2000). Pan and Sano (2000) reported for different lignins from wheat straw higher values for the  $M_n$  and  $M_w$  of respectively 1800 – 2000 and 3300 – 4400 Daltons. These lignins were acetylated before dissolving in THF. The differences found may be related to the analytical methods used and the applied extraction procedure of the lignin.

Fig. 9. Weight average molecular weight of several lignins determined by different HPSEC methods

Fig. 10. Number average molecular weight of several lignins determined by HPSEC and VPO

Fig. 11. High-performance size-exclusion chromatograms of different lignins

## 5. Conclusions

Despite some contradictory results between different analytical methods used, a number of reproducible and reliable protocols have been established for the characterisation of sulphur-free lignins. From the obtained data for chemical composition and functional group content discerning qualitative features can be derived for application development. Protocols used for determination of the chemical composition, such as lignin, sugar residues, ash, nitrogen and silicates, phenolic hydroxyl and carboxyl groups by non-aqueous titration with TnBAH of alkaline lignins from annual fibres give reliable results.

Alkaline lignins from straw, hemp and flax have a lignin content above 80%, sugar residues up to 3.2% and a nitrogen content up to 1.6%. Obviously, if all nitrogen is present in the form of protein, considerable amounts (<10%) are present. The composition of the sugar residues in these soda lignins is depending on the genetic origin of the starting vegetable fibre material. The ash and silicate content of these lignin samples is ranging between 1.9 – 4.9% and 0 – 0.9% respectively. Non-aqueous titration with TnBAH gives the most reliable and reproducible results for the phenolic and carboxylic groups content of lignin, because the solubility of lignin is highest in the selected solvent. Alcell<sup>TM</sup> lignin has a higher phenolic hydroxyl content and a lower number of carboxyl groups than the soda lignins. Because acetylation of syringic acid and the lignins examined seems incomplete, the determination of the total hydroxyl content is not fully reliable. The ratio of phenolic/aliphatic hydroxyl of lignin is rather difficult to measure accurately with both wet chemical and spectroscopic methods.

$M_n$  and  $M_w$  determination using HPSEC with different solvents, like DMF and THF, gives no inter-laboratory comparable and reliable results for the round robin lignins, which was also found as result of a previously performed round robin in 1992. VPO indicates that flax, hemp and Alcell<sup>TM</sup> lignins have comparable molecular weights of about 600 Daltons, whereas straw lignin has a higher molecular weight of approximately 1400 Daltons. These values for the number average molecular weights are considered to be rather low (2-3 phenylpropane units).

Soda lignins from flax, hemp and straw have a different composition, functional groups and molecular weights as compared to Alcell<sup>TM</sup> lignin, which indicates distinguishing structure related properties.

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Table 1.  
Chemical composition of round robin lignins

Components (% w/w)	Straw	Hemp	Flax1	Flax2	Hardwood (Alcell <sup>TM</sup> ) Milne <i>et al</i> 1992	
Total lignin	87.1	85.4	97.6	83.3	96.5	96.2
Klason lignin	86.6	84.7	97.2	82.4	96.1	
Acid-soluble lignin	0.5	0.7	0.4	0.9	0.4	
Total sugar residues <sup>a</sup>	2.39	3.15	1.74	2.09	0.32	0.3
arabinose	0.43	0.30	0.19	0.19	0.00	
xylose	0.72	0.13	0.07	0.08	0.22	
mannose	0.05	0.05	0.07	0.05	0.01	
galactose	0.26	1.10	0.25	0.32	0.00	
glucose	0.75	1.50	1.03	0.72	0.09	
rhamnose	0.08	0.07	0.03	0.03	0.00	
uronic acids	0.1	0.0	0.1	0.7	0.0	
Nitrogen	1.61	1.20	0.76	0.94	0.14	0.2
Ash	1.9	4.5	4.6	4.9	0.1	
Silicates	0.7	0.6	0.9	0.0	0.0	

<sup>a</sup> = sugar residues calculated as polysaccharides

Table 2.  
Solubility (%) of a 2 % (w/w) lignin solution

Solvent	Straw	Hemp	Flax1	Flax2	Hardwood (Alcell <sup>TM</sup> )
DMF + 0.2 mol l <sup>-1</sup> LiCl	99.7	94.5	99.4	89.8	99.9
THF	53.2	76.4	55.2	62.3	100.0

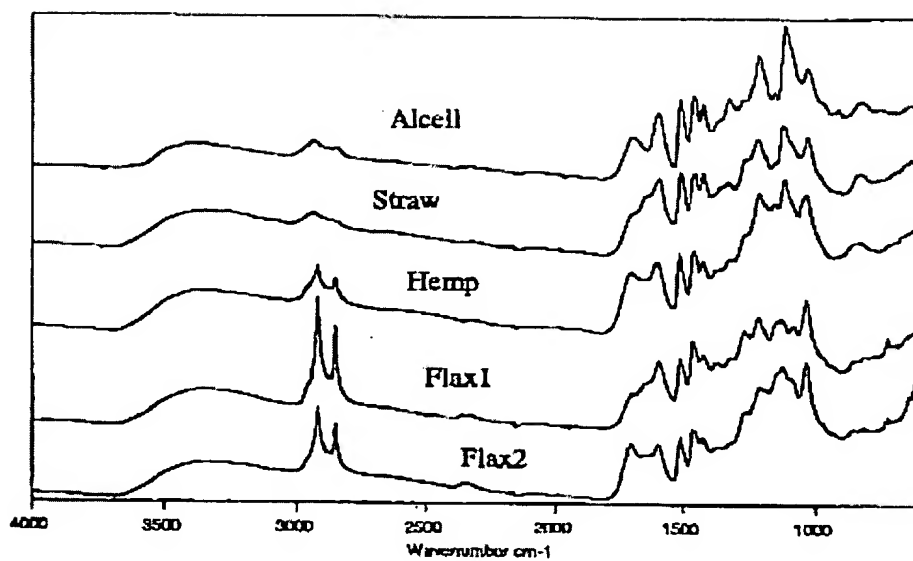


Fig. 1. FTIR spectra of different lignins studied



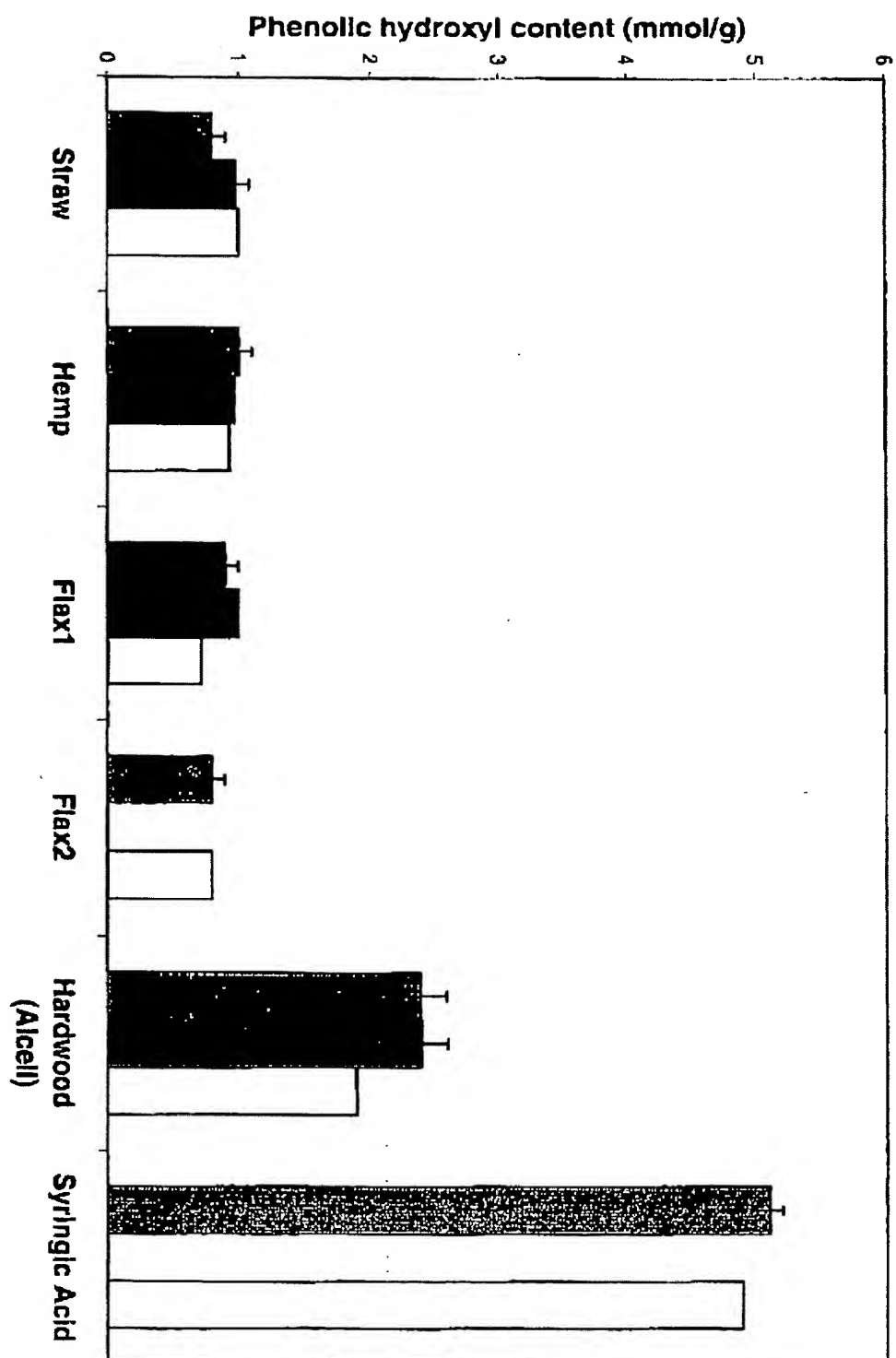


Figure 2

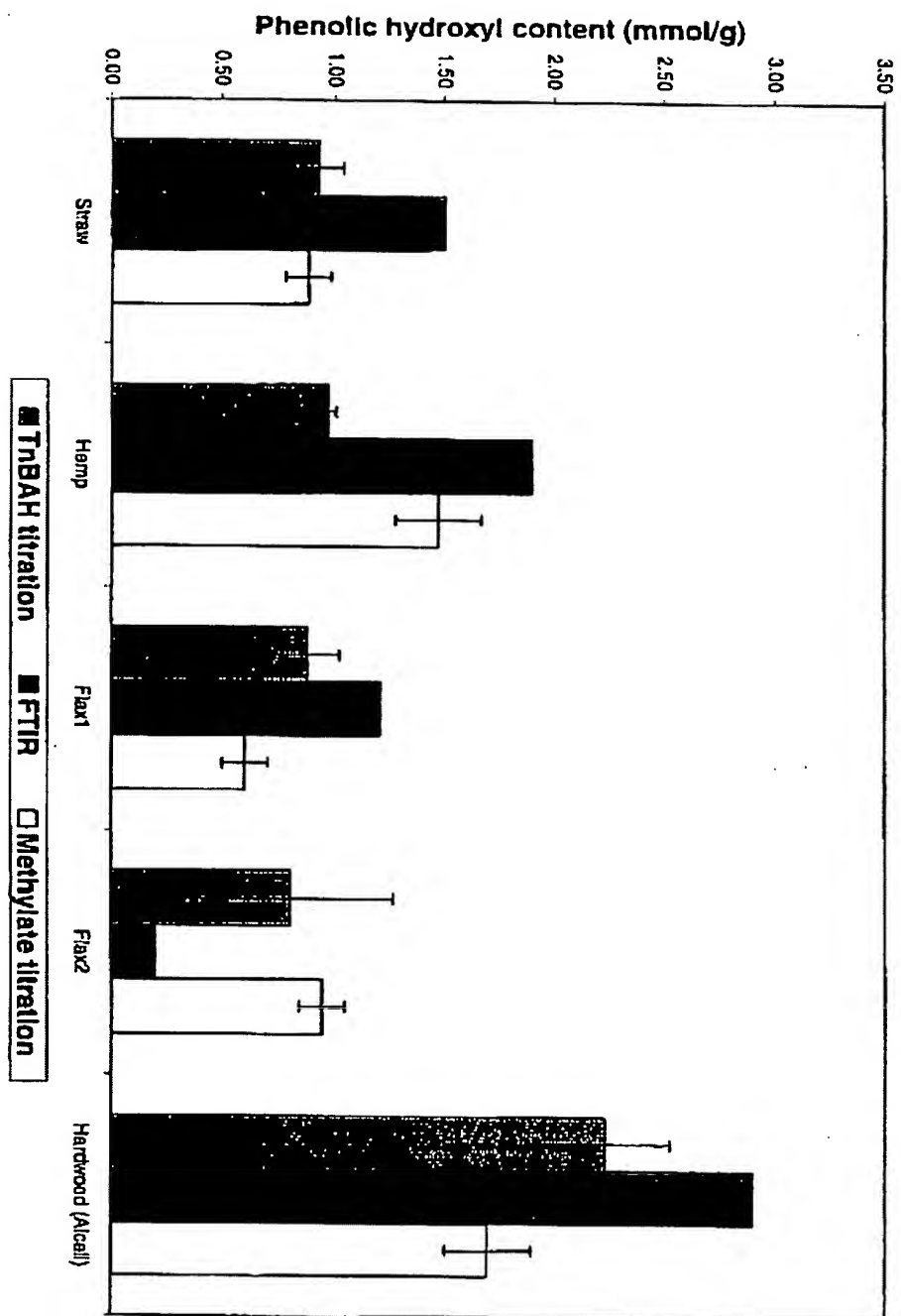


Figure 3.

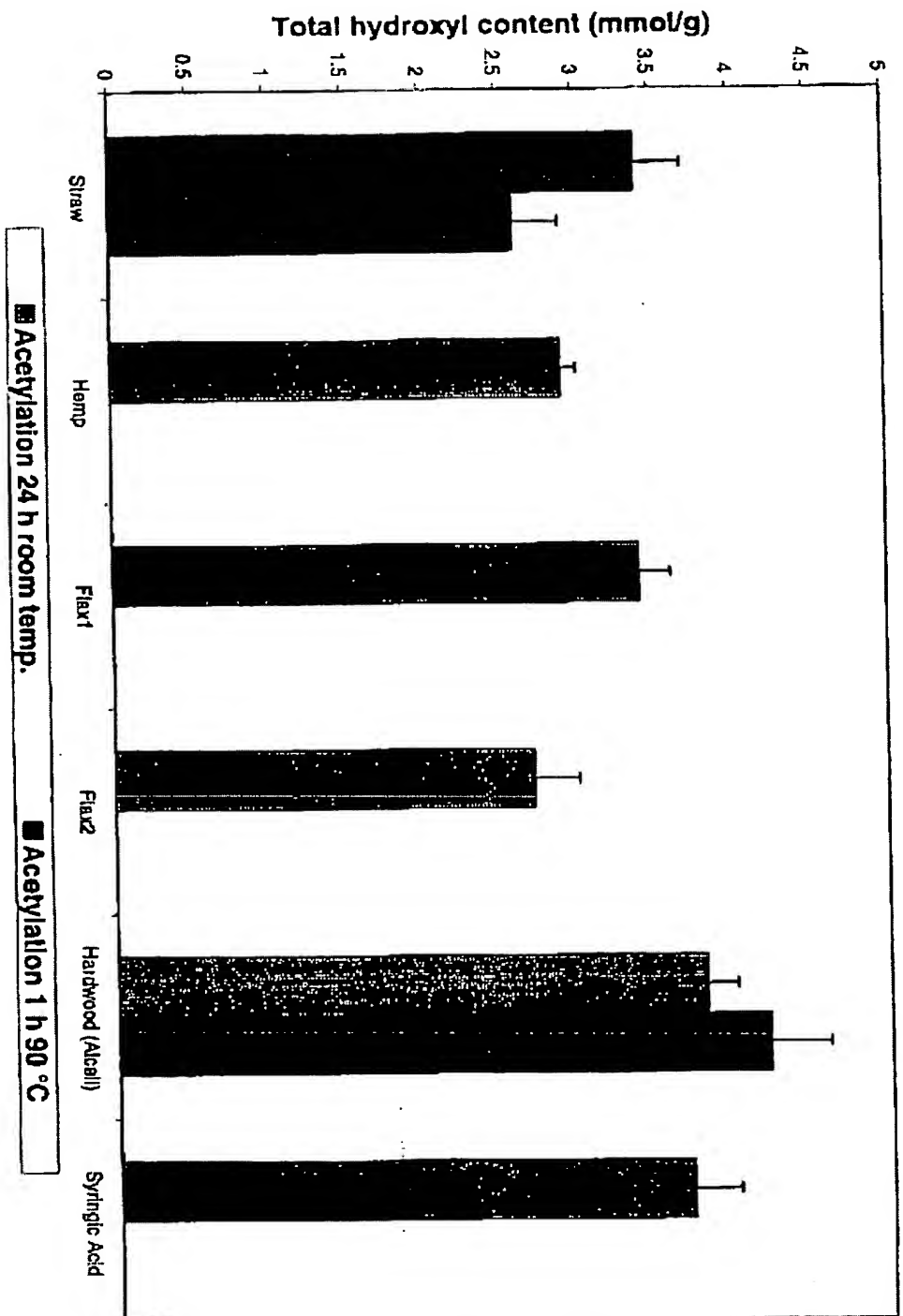


Figure 4

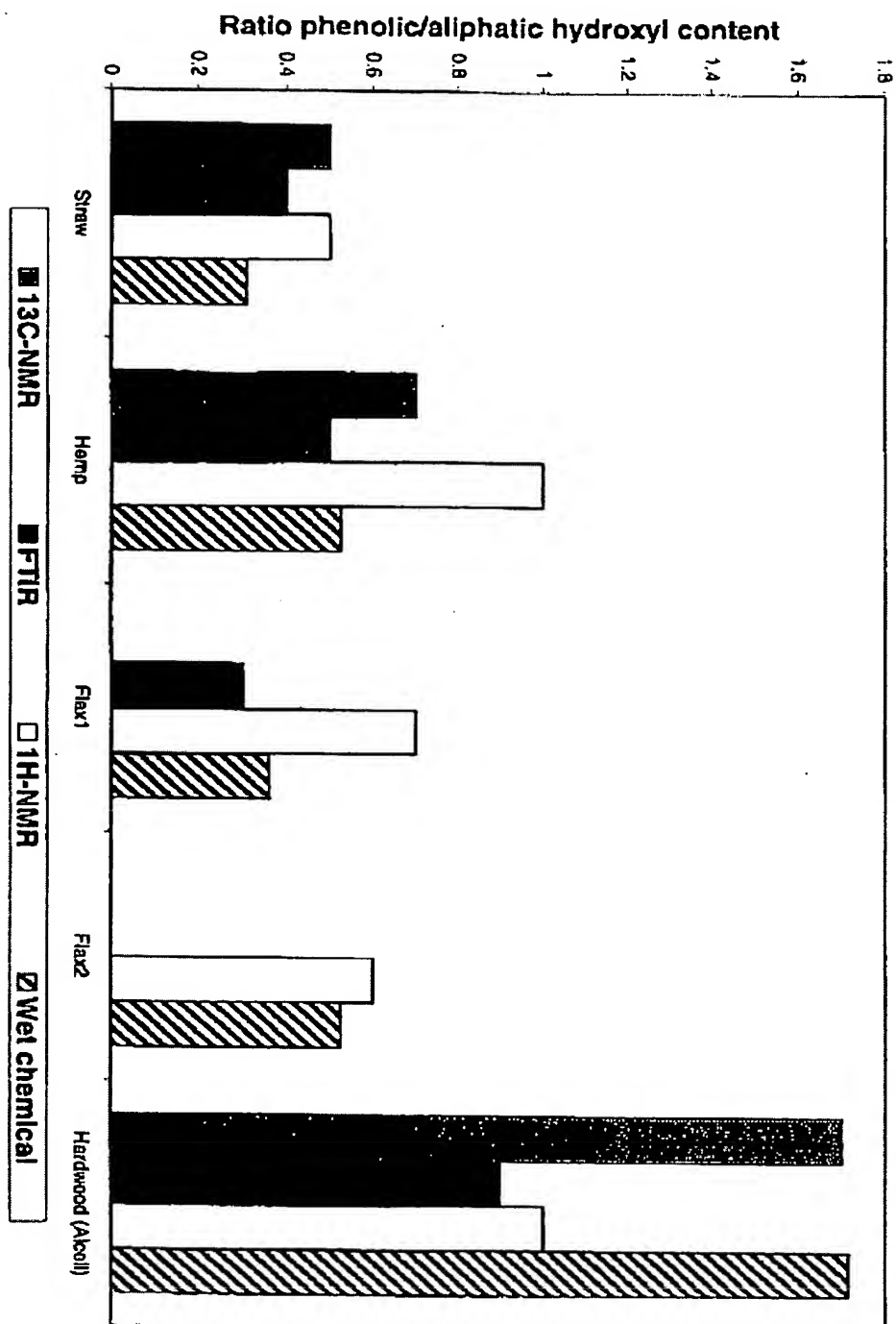


Figure 5

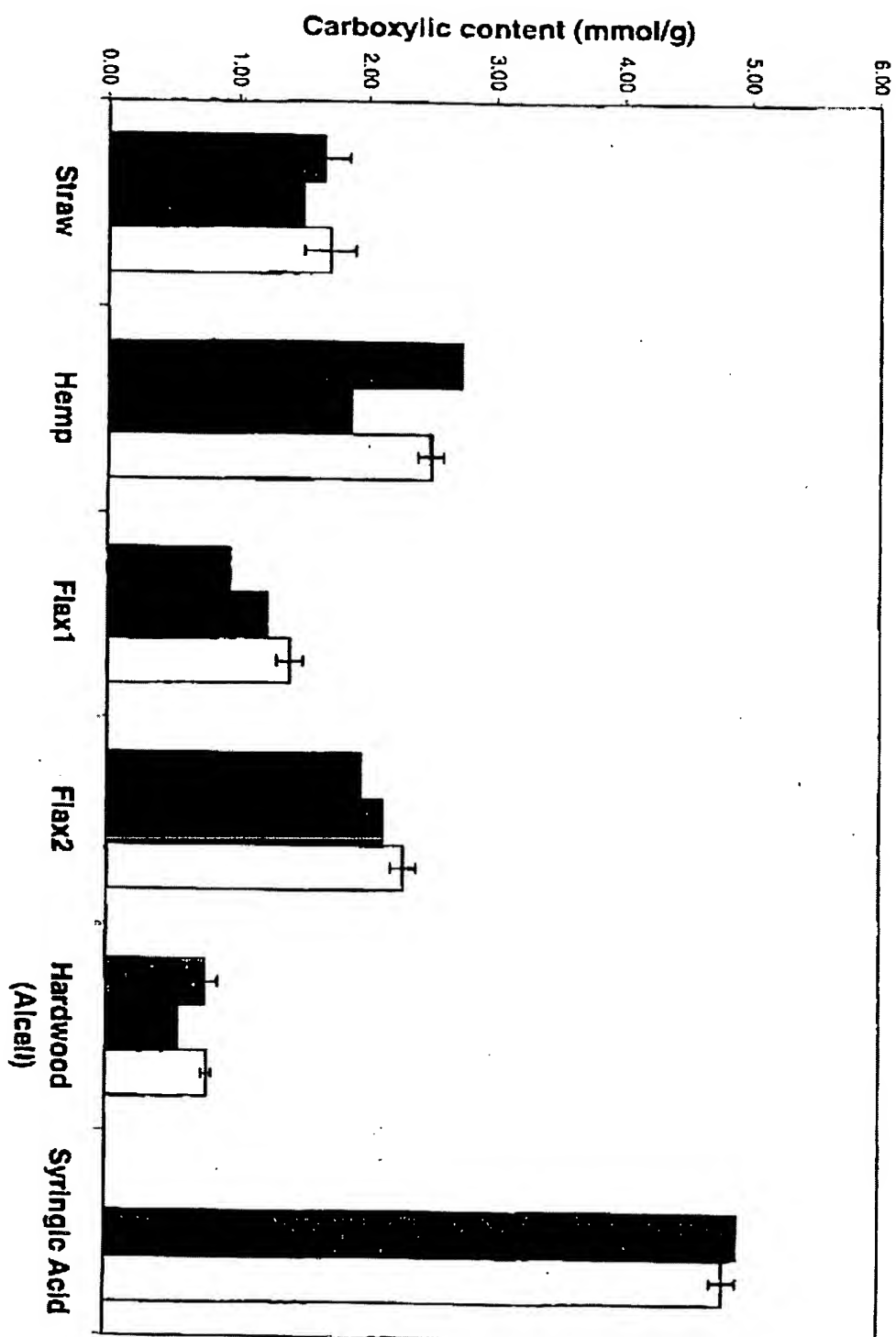


Figure 6

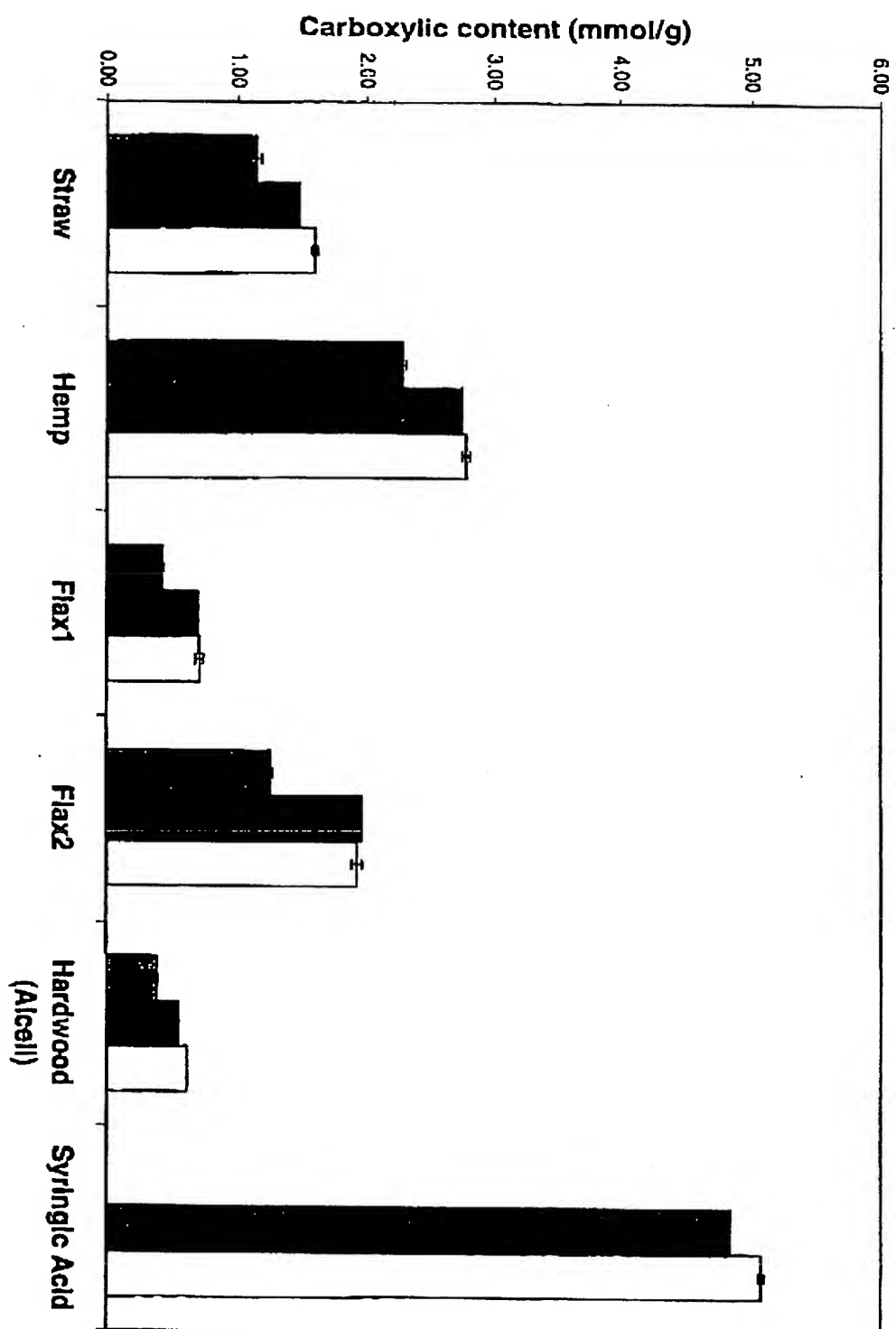


Figure 7

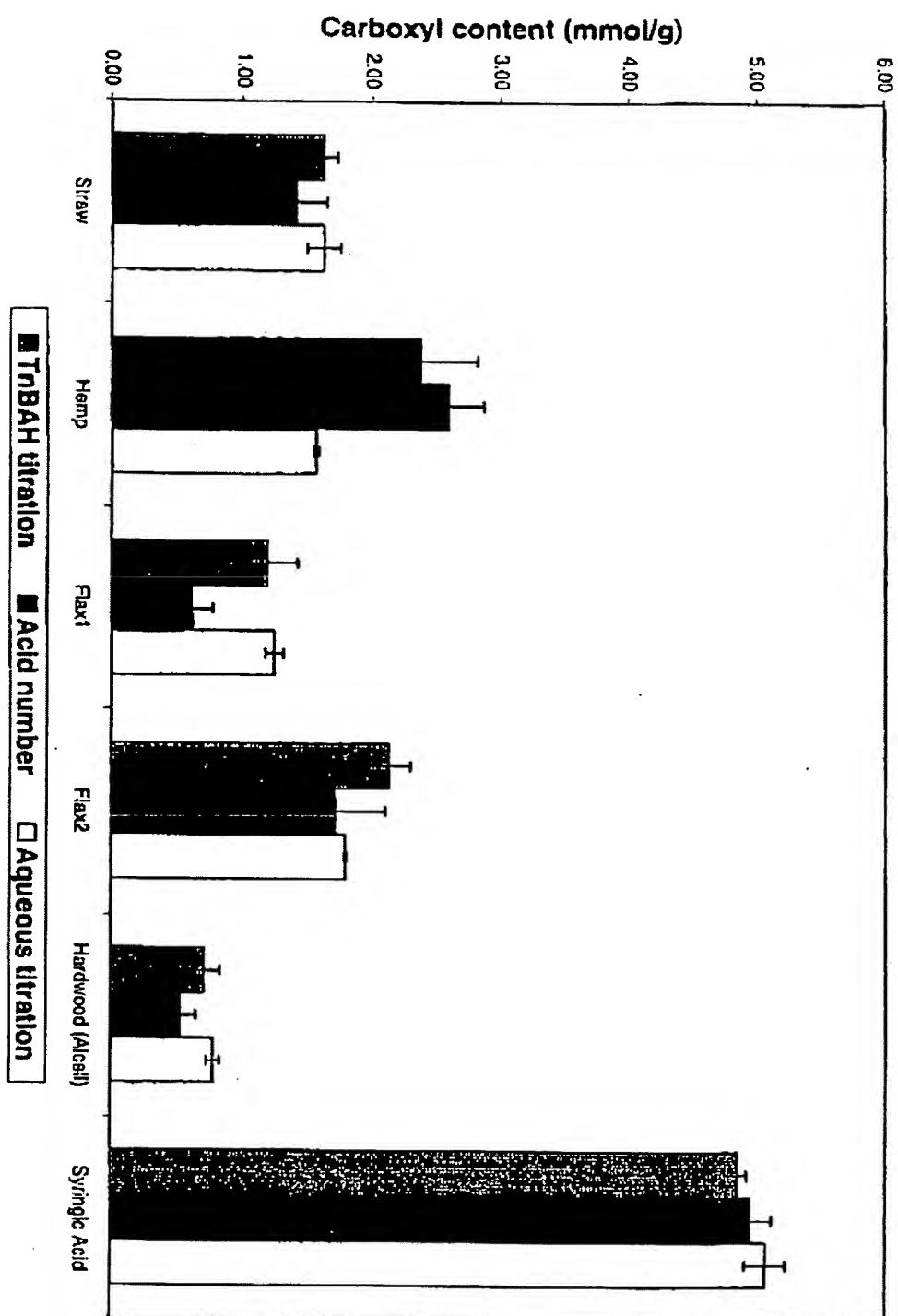


Figure 8

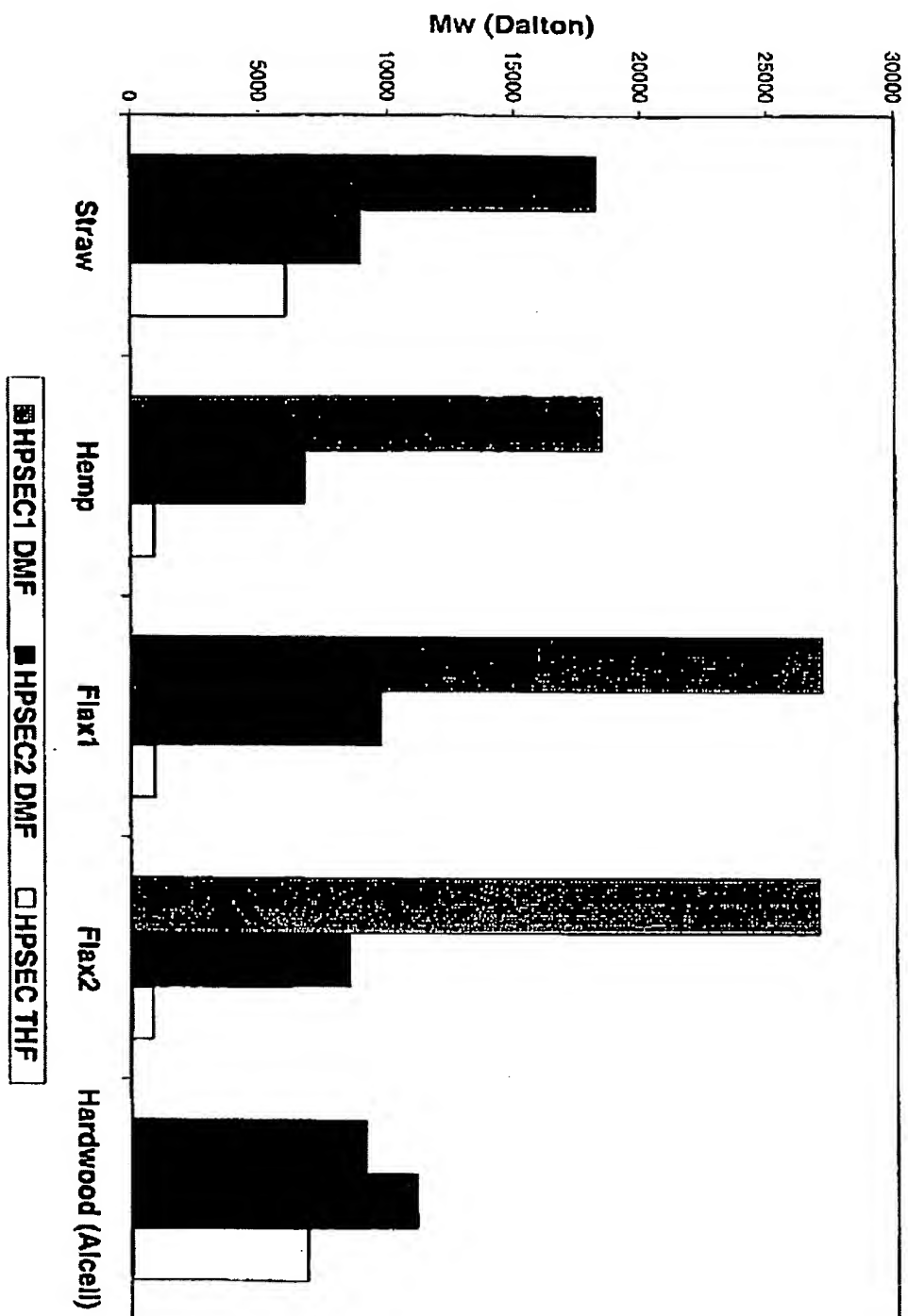


Figure 9.



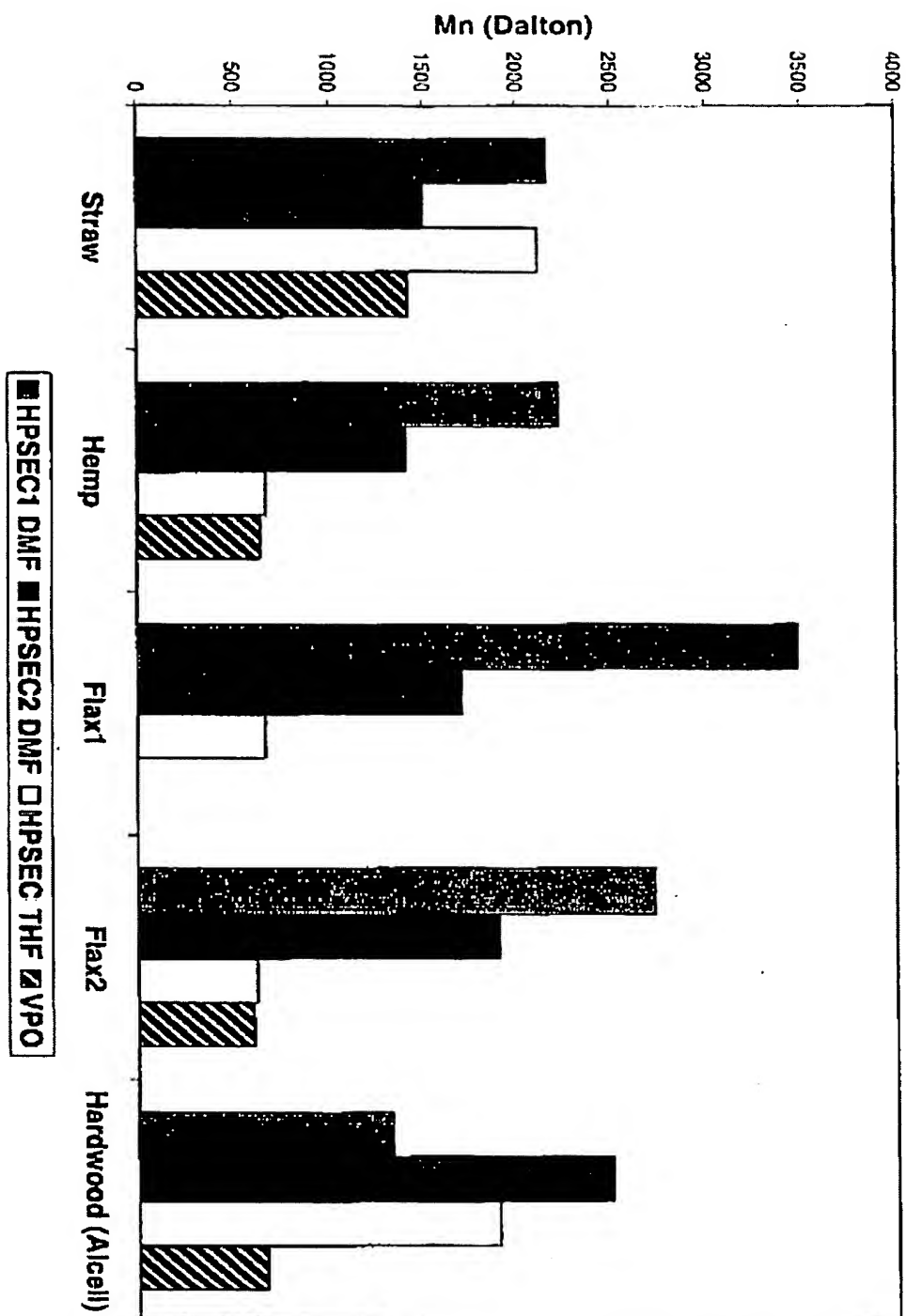


Figure 10

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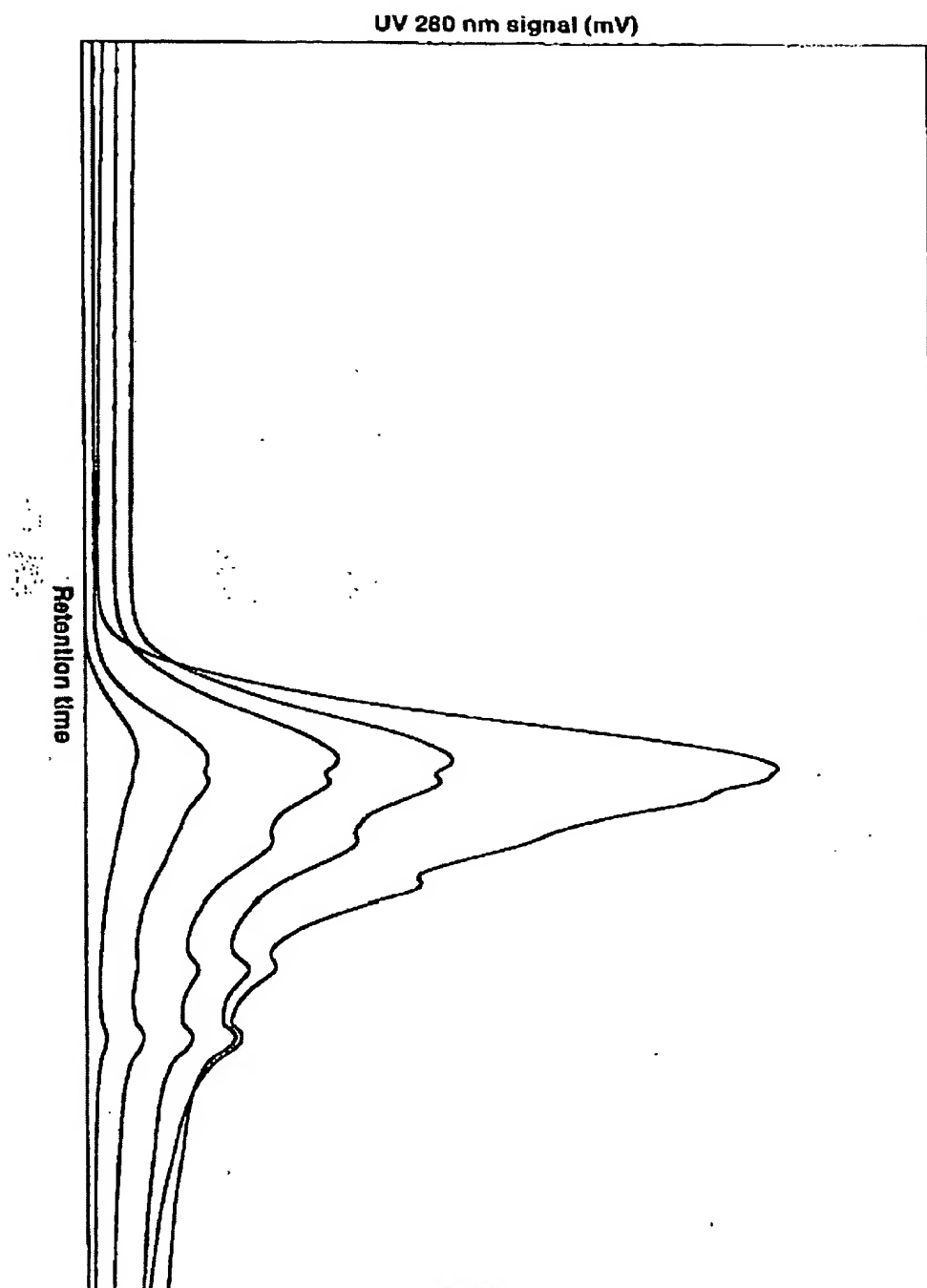


Figure 11

# CHEMICAL MODIFICATION, PROPERTIES, AND USAGE OF LIGNIN

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# CHARACTERISTICS, INDUSTRIAL SOURCES, AND UTILIZATION OF LIGNINS FROM NON-WOOD PLANTS

Jairo H. Lora\*

## 1. INTRODUCTION

Non-wood fibers were the first material ever used by mankind for paper production and had played a dominant role until about one hundred years ago. Today, non-wood fibers such as bagasse and straw remain an important pulping raw material in certain developing countries with limited forest resources. In addition, non-wood fibers such as abaca, sisal, flax, jute, and hemp are used to produce specialty papers in several countries.

When compared with wood, non-wood fibres are at a logistic disadvantage due to their high bulkiness, and the fact that they are produced seasonally, which gives rise to transportation and storage problems. As a result, non-wood fibre mills are normally small in capacity, and can not benefit from the economies of scale enjoyed by wood-based operations.

The vast majority of non-wood fiber mills do not have a recovery system for the pulping chemicals because of the capital-intensive nature of such processes. As a result, the spent pulping liquors are an environmental liability. Although for many years mills have been allowed to release the liquors into the environment with little or no treatment, the situation is changing. China and India, the main producers of non-wood pulps are enacting legislation to decrease the pollution from small mills. The lignin present in the liquor constitutes a potential co-product that, if recovered, could not only decrease the environmental impact of non-wood pulping operations but also contribute to their financial well being. In this chapter we will review the characteristics of non-wood lignins, their sources and uses.

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## 2. CHARACTERISTICS

Although non-wood lignins have been the subject of considerable less study than lignins from wood, significant progress has been made in the understanding of their native structure. From the standpoint of chemical composition, non-wood lignins are more complex than their wood counterparts. Softwoods contain predominantly guaiacyl-type lignins and hardwoods possess a mixture of guaiacyl and syringyl-type lignins, while most non-wood lignins have significant amounts of p-hydroxyphenylpropane nuclei in addition to syringyl and guaiacyl units.

Degradation techniques are often used to infer the type and quantity of aromatic nuclei in lignins. Thioacidolysis and nitrobenzene oxidation are analytical methods that give estimates of the type and abundance of the aromatic nuclei involved in units linked by  $\beta$ -O-4 bonds and in non-condensed units, respectively. Tables 1 and 2 illustrate the results obtained when various authors applied these techniques to a range of non-wood lignins, either *in situ* or after isolation. As can be seen, the proportion of the three types of nuclei varies for different non-wood species. While kenaf and jute are high in non-condensed syringyl units, and have low, or lack, p-hydroxyphenylpropane, wheat straw and bagasse are high in p-hydroxyphenylpropane and have syringyl and guaiacyl non-condensed units in roughly equal quantities. The data also illustrates the fact that for a given species there is variability depending on cultivar type and on the specific part of the plant.

Table 1. Molar ratios of syringyl (S), guaiacyl (G), and p-hydroxyphenylpropane (H) units upon thioacidolysis of non-wood lignins

Species	S	G	H	Ref
Wheat straw cv. Champlain - <i>in situ</i>	46	49	5	1
Wheat straw cv. Capitole - <i>in situ</i>	53	43	4	1
Wheat straw - alkali soluble	55	40	5	2
Wheat straw - <i>in situ</i>	45	49	8	3
Rice straw cv. Balilla norm. - <i>in situ</i>	40	45	15	1
Rice straw cv. Balilla brittle - <i>in situ</i>	47	45	8	1
Kenaf - bast fibers - cv. Everglades	78	22	n. d.	4
Kenaf - inner bast - cv. Everglades	60	40	n. d.	4
Kenaf - woody core - cv. Everglades	58	42	n. d.	4
Kenaf - bast fibers - cv. Aokawa-3	79	21	n. d.	4
Kenaf - inner bast - cv. Aokawa-3	60	40	n. d.	4
Kenaf - woody core - cv. Aokawa-3	58	42	n. d.	4
Kenaf - bast fibers - cv. Metsa	71	29	n. d.	4
Kenaf - inner bast - cv. Metsa	70	30	n. d.	4
Kenaf - woody core - cv. Metsa	66	34	n. d.	4
Kenaf - cell wall preparation	84	16	n. d.	5

n. d. = not detected.

Table 2. Molar ratios of syringyl (S), guaiacyl (G), and p-hydroxyphenylpropane (H) nitrobenzene oxidation products

Species	S	G	H	Ref
Wheat straw internodes - <i>in situ</i>	45	46	9	4
Wheat straw nodes - <i>in situ</i>	52	36	13	5
Wheat straw - alkali soluble	46	43	11	2
Wheat straw - cell wall residue	37	41	22	2
Wheat straw - milled straw lignin	37	48	15	7
Wheat straw - <i>in situ</i>	43	50	7	3
Wheat straw - milled straw lignin	34	51	15	2
Wheat straw - <i>in situ</i>	33	52	15	8
Wheat straw - milled straw lignin	43	49	8	9
Wheat straw - alkali soluble	48	48	4	9
Wheat straw - acetic acid lignin	45	44	11	9
Bagasse - Kraft lignin	35	38	27	10
Kenaf - bast fibers	79	20	1	11
Kenaf - woody core	66	31	3	11
Kenaf - bast fibers - cv Everglades	79	21	n. d.	1
Kenaf - inner bast - cv. Everglades	58	42	n. d.	2
Kenaf - woody core- cv. Everglades	57	43	n. d.	1
Kenaf - bast fibers - cv Aokawa-3	50	20	n. d.	4
Kenaf - inner bast - cv. Aokawa-3	60	40	n. d.	2
Kenaf - woody core- cv. Aokawa-3	58	42	n. d.	4
Kenaf - bast fibers - cv Metsa	68	32	n. d.	4
Kenaf - inner bast - cv. Metsa	72	28	n. d.	4
Kenaf - woody core- cv. Metsa	66	34	n. d.	4
Hemp - bast fibers	47	53	n. d.	12
Hemp - woody core	44	56	n. d.	12
Jute - woody core	58	42	n. d.	13
Jute - bast fibers	67	33	n. d.	13

n. d. = not detected.

There is a general agreement in the literature that in bamboo, and in grasses, such as wheat straw, sugar cane bagasse, and reed canary grass, among others, the majority of the *p*-hydroxyphenylpropane units appear as *p*-coumaric ester groups linked to the lignin core structure.<sup>9, 14-17</sup> Recent work has established that the ester linkage is exclusively connected to the  $\gamma$ -position of the lignin aliphatic chain.<sup>18</sup> A smaller proportion of *p*-coumaric acid groups is connected to the lignin via ether groups or carbon-to-carbon bonds. Other phenolic acids such as ferulic acid esters and ethers are also incorporated in certain non-wood lignin.<sup>19, 19-21</sup>

Phenolic acids etherified to the lignin are a crosslinking bridge for cell wall polymers, since such acids can also be attached to the carbohydrates via an ester link.<sup>21, 22</sup> Such lignin-carbohydrate complexes are very abundant in certain non-woods. For instance, most of the lignin in rice straw is chemically bonded to the hemicelluloses, according to Yu et al.<sup>24, 25</sup> The occurrence of lignin-carbohydrate complexes presents a challenge for the industrial production of high purity lignins.

Another structural feature that may occur in native non-wood lignins is acylation. For instance, according to Ralph, kenaf lignin is about 50% acetylated.<sup>16</sup>

Based on degradation studies, inferences can be made about the degree of condensation of *in situ* and isolated lignins. Thus, wheat straw lignins have fewer  $\beta$ -O-4 linkages and are more condensed (i.e., have more carbon-to-carbon bonds) than those from wood.<sup>2, 22</sup>

NMR and FTIR have been used to elucidate the structure of non-wood lignins. Most of the <sup>13</sup>C NMR work found in the literature has been of a qualitative nature, including studies on wheat straw<sup>21</sup>, jute<sup>13</sup> and bagasse.<sup>14, 23</sup> Quantitative <sup>13</sup>C NMR techniques have been used to estimate condensed and non-condensed aromatic nuclei in rice straw lignin. The results show S:G:H ratios of 24:34:42 for the non-condensed units, and 20:44:36 for the total (condensed + non-condensed) nuclei.<sup>29</sup> Wheat straw lignins before and after biodegradation have been characterized by <sup>31</sup>P NMR, a technique that gives a good quantitative picture of the nature of the different hydroxyl groups present.<sup>20</sup>

Compared with the work on native non-wood lignins, a lot less has been published on the properties of non-wood lignins recovered from industrial black liquors. Properties such as chemical functionality, purity, and molecular weight play a significant role in determining performance in (and suitability for) specific applications. These parameters are determined not only by the structure and characteristics of the native lignin, but also by the pulping and lignin recovery processes. Table 3 shows the data on aliphatic (R) and aromatic (Ar) hydroxyl, carboxyl, and methoxyl group for non-wood lignins obtained from pulping liquors from various commercial and semi-commercial processes. The hydroxyl and carboxyl groups are very instrumental for the chemical modification of lignin for various industrial uses.

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Table 3. Functional groups in selected non-wood lignins (moles per lignin C<sub>6</sub> unit)

Species	Pulping Process	R-OH	Ar-OH	COOH	OCH <sub>3</sub>	Ref
Wheat straw	Soda	0.26	0.38	0.28	0.71	21
Wheat straw	Soda	0.68	0.56	0.35	0.89	22
Wheat straw	Soda-AQ	0.87	0.75	n. m.	1.02	9
Wheat straw	Alkaline Sulfite with AQ and formaldehyde	n. m.	n. m.	0.26	n. m.	23
Wheat straw	Solvent (Acetic Acid)	0.65	0.59	n. m.	1.02	9
Wheat straw	Solvent (Alcohol)	0.61-0.82	0.39-0.65	0.09-0.12	0.75-0.79	24
Hemp	Soda	0.57	0.49	0.14	0.86	25
Bagasse	Kraft	n. m.	0.51	0.21	0.85	12
Bagasse	Autohydrolysis Extraction	0.34	0.44	n. m.	0.56	26
Bagasse	Solvent (Acetic Acid)	n. m.	0.77	n. m.	0.80	26
Reed	Solvent (Alcohol)	0.52-0.56	0.50-0.62	0.08-0.09	0.95-1.01	24
Kenaf (whole)	Solvent (Alcohol)	0.76	0.47	0.04	1	27
Kenaf (core)	Solvent (Alcohol)	0.58	0.45	0.09	0.95	27

n. m. = not measured.

Wheat straw lignosulfonates from alkaline sulfite pulping in the presence of AQ and formaldehyde have a high sulfonic acid content (about 0.83 mol per C<sub>6</sub> unit) with nearly 80% on the side chain and the balance on the aromatic ring.<sup>22</sup>

The non-substituted C-3 and C-5 aromatic positions of the lignin molecule are important for lignin derivatization since those are the sites where alkali-catalyzed aromatic substitution reactions can take place, as needed when trying to increase the reactivity of the lignin by methylation (for instance, for phenolic resins) or methylsulfonation (for dispersants). Data available on this key parameter suggests that some non-wood lignins may have equal or greater number of non-substituted C-3 and C-5 aromatic carbons than softwood kraft, which is considered a benchmark for industrial production of lignin derivatives (See Table 4).



Table 4. Number of non-substituted C-3 and C-5 positions in non-wood lignins and a softwood kraft lignin

Species	Pulping Process	Non-substituted C-3 & C-5 per C <sub>9</sub>	Ref
Bagasse	Soda (mild pulping)	0.7	18
Wheat straw	Soda	0.45	12
Wheat straw	Solvent (Alcohol)	0.64 - 0.83	14
Reed	Solvent (Alcohol)	1.0 - 1.1	14
Pine	Kraft	0.7	32

Another important factor in the potential utilization of lignins is their purity. Non-wood lignins may have three significant extraneous components: sugars, silica and proteins.<sup>21, 40</sup> As discussed earlier, native non-wood lignins may have co-valent bonds with the hemicelluloses. Therefore, it is not surprising to find lignin-carbohydrate complexes in soda pulping liquors,<sup>39</sup> which may lead to the presence of sugars in non-wood lignin preparations. Gosseink et al. reported that soda lignins recovered at the pilot level from industrial black liquors from flax, hemp and wheat straw have 2.1 to 3.2% sugars, 1.9 to 4.9% ash (due in part to silica) and 0.76 to 1.61% nitrogen (equivalent to 4.8 to 10.1% protein).<sup>41</sup> Such levels of contaminants are considered an improvement over soda lignins obtained in the past, which had purity less suitable for value-added utilization.<sup>42</sup> Even higher purity can be attained for non-wood organosolv lignins, which can usually be produced with less than 1.0% sugars and ash.<sup>37</sup>

Other properties of relevance to lignin utilization include molecular weight and thermal characteristics. Although the molecular weight data presented in Table 5 is somewhat scattered, it suggests that non-wood lignins have a relatively low molecular weight, with organosolv lignins at the lower end of the range. A recent round robin among several European labs has identified significant variability in results of molecular weight determinations by size exclusion chromatography for non-wood lignins, which points out to the need for standard procedures in this area.<sup>43</sup>

Lignosulfonates obtained by alkaline sulfite pulping of wheat straw in the presence of formaldehyde and AQ are also reported to have lower molecular weight than wood lignosulfonates and methylsulfonated kraft lignins.<sup>33</sup>

Little information has been published on the thermal properties of non-wood lignins. The data in Table 6 suggests that soda lignins have a higher glass transition temperature than organosolv lignins, which is probably related to the lower molecular weight of the latter. Abächerli has recently reported that alkali flax, sisal, abaca, and jute lignins exhibit thermal flow at 120 to 180 °C.<sup>46</sup>

Table 5. Weight ( $M_w$ ) and number ( $M_n$ ) average molecular weight of selected non-wood lignins

Species	Pulping Process	$M_n$	$M_w$	Ref
Wheat straw	Soda	1400	1200	32
Wheat straw	Soda	Not reported	1400	41
Wheat straw	Soda-AQ	3270	1770	9
Wheat straw	Solvent (Acetic Acid)	4430	2020	3
Wheat straw	Solvent (Alcohol)	Not reported	800	43
Flax	Soda	Not reported	600	41
Hemp	Soda	Not reported	600	41
Bagasse	Solvent (Acetone)	2740	840	14
Bagasse	Solvent (Acetic Acid)	Not reported	830	16
Bagasse	Autohydrolysis	4360	420	42
Reed	Solvent (Alcohol)	1410-1480	650-680	34

Table 6. Glass transition temperature of selected non-wood lignins

Species	Pulping Process	Glass Transition Temperature, °C	Ref
Wheat straw	Soda-AQ	160 (crude), 185 (purified)	9
Wheat straw	Solvent (Acetic acid)	142 (crude), 172 (purified)	9
Bagasse	Solvent (Acetic acid)	170	16
Hemp	Soda	158 (1 bar), 103 (20 bar)	34
Reed	Solvent (alcohol)	96 - 97 (1 bar), 63 - 72 (20 bar)	34
Wheat straw	Solvent (alcohol)	106 - 122 (1 bar), 61 - 89 (20 bar)	34
Kenaf	Solvent (alcohol)	66 - 70 (1 bar), 104 - 108 (20 bar)	37

### 3. INDUSTRIAL SOURCES

Most industrial non-wood pulping is done with alkaline processes, including the soda, soda-AQ, alkaline sulfite, and kraft processes. Soda and soda-AQ are the predominant processes, since in general non-wood fibers are easy to delignify because of their relatively low lignin content and their accessible morphology. Soda pulping is almost always employed for the most widely used feedstocks such as sugarcane bagasse and wheat straw. The alkaline sulfite process is often used to pulp specialty fibers such as abaca, flax, and hemp. In some countries some non-wood mills switch pulping processes depending on the relative price of sodium sulfite and caustic soda. The kraft process is used commercially for bamboo and kenaf.

The liquors potentially available for lignin recovery are primarily from small soda mills that cannot afford a recovery system and that may be under pressure to either treat their effluent or close down. A second source is larger mills that may have a recovery process but want to incrementally expand their pulping capacity and need an economic way to handle the excess liquor generated.

Several researchers have proposed lignin recovery from soda black liquors as a strategy to diminish the Chemical Oxygen Demand (COD) of the effluents. The proposed processes typically involve lignin precipitation by acidification followed by liquid solids separation.<sup>47,50</sup> One of the difficulties of this procedure when dealing with non-wood fibers is that the spent liquors from alkaline pulping often contain silica, which may co-precipitate with the lignin, rendering it of lower quality. According to Gratzl and Chen,<sup>51</sup> precipitation processes used in Asia have not been successful to separate lignin from silica. The LPS® precipitation process recently introduced commercially in Europe is claimed to have solved this problem and to have obtained soda lignins with relatively low ash and silica content.<sup>51</sup>

Although lignin recovery eliminates a substantial portion of the effluent load, it is by no means a complete solution to the environmental problems of non-wood mills, and additional treatment may be required to achieve acceptable discharge limits. Fortunately, the remaining effluent appears to be amenable to biological treatment. Indian and Chinese researchers have reported on the successful biodegradation of such an effluent with anaerobic as well as photosynthetic organisms.<sup>52,53</sup>

In the case of alkaline sulfite pulping liquors, Chinese researchers have also proposed lignin removal by acidification with sulfur dioxide<sup>54</sup> or with sulfuric acid<sup>55</sup> as an effective way to reduce the pollution load. Surprisingly good results are claimed, in spite of the more hydrophilic nature of the lignin present in these liquors.

One further variant on alkaline sulfite pulping involves the use of formaldehyde and anthraquinone as pulping additives, which leads to the formation of highly sulfonated lignins in the spent liquors.<sup>56, 57</sup> It is doubtful that a pulping method involving formaldehyde could have widespread industrial use, but the liquors obtained have properties suitable for a variety of applications and, therefore, whole liquor utilization has been proposed as a preferred way for disposal.

More recently, novel pulping processes have been proposed for processing non-wood fibres. For instance, autocatalyzed organosolv pulping is reported to be particularly suitable for non-wood fibers, since this technique is suitable for small scale operation, given the simplified recovery process, immunity to silica accumulation problems, and the generation of high purity co-products, such as lignin. One example of autocatalyzed solvent pulping is the Alcell® process, in which aqueous ethanol is used as the pulping medium and lignin is recovered by precipitation by adjustment of the solvent concentration, the pH, and temperature of the spent cooking liquor. This process has been proposed for wheat straw, reed, kenaf, and sugar cane bagasse among others.<sup>57, 58-60</sup> Other organosolv processes that have been proposed for non-wood fibres and offer the potential of lignin recovery include pulping with organic acids.<sup>61-63</sup> In spite of the promise offered by organosolv pulping processes, their commercial implementation has not yet occurred.

Biomass fractionation technologies have also been tried on non-wood fibers and can potentially generate lignins of interesting properties. Autohydrolysis of biomass (i.e.,

treatment with water or steam at high temperature without added catalysts) can be used to solubilize hemicelluloses (which can be further converted to furfural) and generate a residue from which lignin can be extracted with solvents or dilute alkali.<sup>64</sup> A South African company developed a lignin called Sucrolin from residues from industrial furfural production from sugar cane bagasse in the 1980's.<sup>65</sup> A similar process, based on steam explosion can also be used to obtain an alkali extractable lignin from biomass. This is under investigation on wheat straw at the pilot level in Italy.<sup>66</sup>

Regarding the commercial availability of non-wood lignins, there are several suggestions in the literature on the industrial implementation of the precipitation of soda lignin in Asia for environmental management reasons.<sup>67-69</sup> It is not known if lignin recovered in such operations is currently being marketed. Concerning Europe, in the Fall of 2000 a lignin recovery plant using the LPS® process started operating at a small flax pulping mill in France. This unit has started generating lignins in solution and powder form for a range of industrial markets.<sup>70</sup>

#### 4. UTILIZATION

Perhaps because of the difficulties encountered in efficiently recovering high quality lignins from non-wood fibers,<sup>42</sup> some of the attempts for lignin utilization have included the direct use of the liquors without much further processing. Chinese researchers have identified the potential use of black liquor from soda cooking of wheat straw, rice straw, and Chinese alpine rush in tertiary oil recovery. Black liquor flooding was found to be similar to alkali flooding, but followed a much more complicated mechanism due to its more complex composition.<sup>71, 72</sup> Concentrated and spray-dried black liquors have been used to manufacture gels to reduce the permeability of underground strata and thus aid in the recovery of oil by steam flooding. The gel manufacture process involves a reaction with phenol, formaldehyde and a crosslinking agent. Partially hydrolyzed polyacrylamide and activated clay can be added to improve viscoelastic properties. The gels obtained had good strength properties and were stable to heat (250 °C for at least 168 h), water, salt, caustic and acid. Lignin-based gels were tested in 10 oil wells in China in 1991-1992 and found to be capable of increasing oil output with a useful life of six months.<sup>73, 74</sup>

One of the approaches that have been attempted for lignin utilization involves the direct use of spent liquors in agriculture. Thus, liquors from ammonia-sulfite pulping have been tried for irrigation and fertilization, but efforts in this direction have proven to be impractical due to seasonal demand considerations.<sup>42</sup>

Although the use of whole liquors may be feasible and justified under specific circumstances, the use of isolated lignins is what offers the potential for most widespread and versatile utilization. One current effort on the use of lignins recovered from existing pulp mills is the Valoir project, which is a consortium of nine industrial companies and research institutions, partially funded by the European Community. This consortium is pursuing the use of non-wood lignins as emulsifiers,<sup>75</sup> as components of thermoplastics,<sup>75</sup> and in the concrete and wood panels industries.

Non-wood lignins have been evaluated as additives for the manufacture of biodegradable, starch-based plastic materials for packaging and other applications. For instance, the use of Alcell® wheat straw lignin in starch composite films results in an improvement in water resistance properties of the films and in certain plasticizing

effects.<sup>43</sup> An extension of this work to alkaline lignins has shown that wheat straw and hemp lignins can reduce the glass transition temperature of starch/glycerol films by 60-70%.<sup>44</sup>

Lignin has several reactive groups that can be used for modification reactions to obtain useful derivatives. Since lignin from wood is almost exclusively marketed as sulfonated derivatives (either lignosulfonates or methylsulfonated kraft) the conversion of isolated non-wood lignins to sulfonated derivatives has been the focus of research and development efforts.

Straw soda black liquor and lignin isolated therefrom were sulfonated to produce water reducers for concrete (i.e., dispersants that allow the use of less water when making concrete, which results in a stronger product). The product obtained from the sulfonated liquor was similar in performance to wood-derived calcium lignosulfonate, while the sulfonated lignin product performed similar to naphthalene-sulfonate, which is considered a high-quality water-reducer.<sup>74</sup>

The reactivity of soda straw lignin and pine kraft lignin in methylsulfonation and sulfonation were compared by He *et al.*<sup>53</sup> Significant differences between the two types of lignins were noticed in methylsulfonation, with pine kraft lignin being much more reactive than straw lignin. This is attributed to the higher number of non-substituted ortho positions to the phenolic OH (i.e., C-3 and C-5) in the former. In the case of high temperature sulfonation, straw and pine lignins behaved similarly. Regardless of its lower reactivity, it was possible to generate from straw soda lignin products with excellent water solubility characteristics and superior dispersing properties. For instance, at the same sulfonation level, straw lignin had lower surface tension than kraft lignin, probably because of the higher carboxylic acid content of the non-wood lignin. A methylsulfonation pilot plant for bamboo with a capacity of 2 tons per day was built in China in 1992.<sup>42</sup>

Reed lignosulfonates have been grafted with acrylic acid using a redox copolymerization initiated with peroxide in a one-step as well as in a continuous process. The products obtained have potential use as water treatment chemicals, with the higher molecular weight products exhibiting better dispersing properties.<sup>75</sup>

Modified lignosulfonates obtained by pulping straw with sodium sulfite in the presence of formaldehyde are characterized by their high degree of sulfonation (4.15 mmol of sulfonic acid groups per gram of lignin) and low molecular weight. Their application in drilling muds and as dispersants (for instance, for titanium dioxide) has been studied by Chinese researchers.<sup>53, 60</sup>

Given its aromatic structure and renewable nature, lignin has been extensively evaluated as a partial replacement for phenol in the manufacture of phenolic resins. Studies on the utilization of bagasse soda and autohydrolysis lignins in phenolic resins have shown that a number of strategies can be employed to activate the lignin molecule and enhance its reactivity. These include methylation, phenolation, methylation followed by reaction with phenol or resorcinol, and reacting with pitch residues from coal gasification. Depending on the modification method employed, the resulting phenolic polymers can be used as cold set adhesives, thermosets for wood panels, and saturants for paper laminates, among others.<sup>61-67</sup> Bagasse lignins obtained by pulping in acetic acid were successfully used in phenolic molded products up to a 40% phenol replacement level with improvement in mechanical properties. The lignins were shown to chemically react with the phenol polymer chain, acting as chain extender rather than as filler.<sup>66</sup>

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A few authors have reported the preparation and characterization of miscellaneous non-wood lignin derivatives. Thus, bagasse kraft lignin has been graft co-polymerized with maleic anhydride.<sup>40</sup> Brazilian researchers have prepared polyamides by polymerization of organosolv sugarcane bagasse lignin that had been aminated with formaldehyde and ammonia (Mannich reaction).<sup>46</sup> The carboxymethylation of sisal soda lignin was reported by researchers at the Swiss Federal Institute of Technology in Lausanne, who demonstrated good reproducibility and correlation between reaction conditions and product characteristics.<sup>45</sup>

Glasser and Jain acylated sugarcane bagasse autohydrolysis lignin and demonstrated that the derivative had a lower thermal softening temperature relative to the parent lignin. Acylation, therefore, can be used to prepare derivatives capable of thermal flow with polyethylene and with potential use in polymer blends.<sup>44</sup>

In a different approach to the use of lignin in plastics, de Jong et al. have proposed the use of straw soda lignins to dye polyolefins, such as polypropylene, with reactive dyes. The mechanical properties of the polymer were not negatively impacted, with the mechanical stability to UV radiation actually showing an improvement.<sup>90</sup>

Egyptian researchers prepared several rice straw lignin derivatives, including carboxylated (using acetic and propionic acid), cyanoethyl, and amino lignins and evaluated them in a variety of applications. They found that the propionated lignin was very good for paper sizing, and the amino-lignin derivative performed well as a flocculating aid and as an additive to enhance water retention in drilling muds.<sup>91</sup>

Straw lignin has also been tried as a polyol in polyurethane foams manufacture. Straw lignin from alkali oxygen pulping has been reported to have higher aliphatic hydroxyl content than lignin from conventional soda cooks, and therefore has greater reactivity with isocyanates.<sup>92</sup>

Straw soda-AQ lignin was modified to form chelating resins for binding metals.<sup>93</sup> In general the best results were obtained by a modification sequence involving ultrafiltration, acid-catalyzed phenolation, Mannich reaction with various amino acids, and carboxymethylation. The products obtained were found to bind copper preferentially. Another proposed approach to the production of chelants involves the oxidation of sugar cane bagasse lignin obtained by organosolv pulping in acetic acid.<sup>94</sup>

The use of isolated lignins and their derivatives (rather than just crude black liquors) in agriculture has been proposed as a potential large lignin market. For instance, Brazilian and British researchers have shown the advantages of using lignin as a controlled release matrix for herbicides, such as 2,4-D and Ametryn, in several studies using sugar cane bagasse lignin.<sup>45, 95, 96</sup>

Cuban workers have proposed sugar cane bagasse lignin as a soil improving agent.<sup>97</sup> Oxidative ammonolysis (i.e., reaction of lignin with oxygen and ammonia) has been proposed as a procedure to generate nitrogen-rich, partially oxidized lignins. The products are claimed to be effective soil conditioners and slow nitrogen-releasing fertilizers.<sup>42</sup>

Popa et al. found that alkaline flax lignin after nitration increases germination of bean seeds and biomass yield by about 30%.<sup>98</sup> Bagasse soda lignin is used in Cuba as an antidiarrheic for cattle, and apparently there are other medicinal and veterinary products under development, such as an anti-mycotic cream and medicaments for pigs.<sup>99</sup> The area of biological activity of lignins and lignin derivatives is certainly a promising field, and one in which much work remains to be done.

## 5. CONCLUSIONS

Recovery of non-wood lignins from existing pulp mills could alleviate environmental problems, and could contribute to the viability of many small operations. Non-wood lignins are polymers with great potential as chemicals and as materials. Their versatile chemical functionality and wide range of physical properties offer multiple avenues for the development of specialty products. To realize the full potential of non-wood lignins, it is necessary to implement processes that deliver them with high and consistent quality and to increase the understanding of the relationship between their chemical structure and performance.

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## PLANT POLYPHENOLS OF IMPORTANCE FOR HUMUS FORMATION

### A contribution to the Polyphenol Theory

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#### Introduction

Humus or soil organic matter as it is alternatively designated, represents one of the most important natural resources and is of fundamental importance for the fertility of soils. It contains about the same quantity of organically bound carbon ( $22 \times 10^{14}$  kg) as the total of living and fossil biomass on the Earth's surface contain together (about  $21 \times 10^{14}$  kg). Theoretically, humus can contain any of the organic compounds synthesised by plants or animals. By the process of mineralization, part of organic carbon from the plant (and animal) residues is converted into carbon dioxide, part of it is metabolised by soil (micro-) organisms and thereafter converted into their biomass and part is transformed through the processes of biodegradation, re-polymerisation and reactions with soil inorganic constituents to humus, or soil organic matter. Resistant organic compounds with aromatic structure, such as plant polyphenols, belong to the last mentioned category.

There are several theories of humus formation and the polyphenol theory seems to be of particular pertinence when humus formation from forest residues is considered. Therefore the contribution of structural wood polyphenols lignins and those extraneous in nature which are biosynthetically related to lignins to the humus formation is the object of this research.

#### Background

Laval University in Quebec has been the centre of an experimental activity in the last two decades aimed to find an application for the forest residues in form of smaller branches, twigs and foliage, for humus formation. All these materials are lignified and contain important quantities of polyphenols which are biosynthetically related to lignins, such as proanthocyanidins. Forest residues were chipped in form of rammeal chipped wood (RCW) and spread at forest land for study of humus formation. The samples of humus originating from well identified wood species are now available for a comparative study with lignins (and other polyphenols) isolated from the same wood sources.

## **Lignins - structural polyphenols of higher plants**

In botanical sense, lignification is accompanying the specialisation of tissues for transport of fluids, which means with the development of vascular system in plants. Lignification can be regarded as modality adopted by plants for adaptation to life on the ground. Lignin is found in vascular plants such as lycopods, ferns, softwoods and hardwoods and is absent from simpler plants such as algae, mosses, fungi and lichens.

Development of a more perfect excretory system has certainly influenced the development of lignification of plant cell walls. Higher plants can perform the excretion through their root system, through the foliage or they can dispose of such metabolites into the vacuoles (soluble polyphenols, such as anthocyanidins, are accumulated in vacuoles) or directly into the cell walls (the insoluble polyphenols, such as lignins, are deposited in cell walls- therefore they are designated structural polyphenols). This explains a variety of secondary metabolites that are found in higher plants.

### **High lignin contents in woods**

Woody tissues in general have quite high lignin contents since they are composed to a large extent of vascular and sclerenchyma cells, such as tracheids, vessels and fibres. In herbaceous plants, for instance, these elements are "diluted" by other cell types, such as parenchyma cells, which do not have strongly lignified walls and consequently the grasses contain less lignin. Woods contain 18-30 % of lignin. Typical lignin contents for hardwood is 18-25 %, for softwood 25-33 %.

### **General phenylpropanoid metabolism in plants and biosynthesis of lignins in plants**

Lignins are formed from carbohydrates ( formed by photosynthesis from  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) through a shikimic acid pathway. The major step in conversion of shikimic acid, which is the obligate intermediate in aromatic transformation, is leading to aromatic acid pools of lignins and other polyphenols: phenylpropanoid amino acids: L- tyrosine and L-phenylalanine. These upon reduction (reductive deamination) give corresponding cinnamic acid derivatives which upon further reduction yield cinnamic alcohol derivatives: p- coumaryl, coniferyl and sinapyl alcohols, the monomeric lignin precursors, or monolignols. Cinnamic acid derivatives, p-coumaric acid in particular is on the other hand the branching point for the biosynthesis of flavonoids through the chalcone intermediate.

L- phenylalanine is an essential amino- acid in primary metabolism, and it is converted by phenylalanine ammonia- lyase

(PAL) to trans- cinnamic acid. PAL is a key enzyme in the synthesis of various phenolic secondary metabolites, lignins being the most important of them because of their natural abundance. This deamination step catalysed by PAL is a principal step that marks the transition from primary to secondary metabolism in higher plants.

Lignins are formed in vascular plants by dehydrogenative polymerisation of cinnamic alcohol derivatives. The heterogeneity of lignins is reflecting the varying ratios of these monolignols participating in lignin biosynthesis. It is interesting that homogeneous wood species such as softwoods are characterised by "homogeneous" lignins which are commonly designated as guaiacyl G lignins, referring to guaiacyl rings introduced by almost exclusive polymerisation of coniferyl alcohol. Hardwood lignins are designated as guaiacyl- syringyl (G-S), lignin heterogeneity reflecting therefore the heterogeneity of hardwoods in general.

Dehydrogenative polymerisation is enzymatically initiated by laccase and molecular oxygen or peroxidase and peroxide, which leads to formation of resonance hybrids of radicals of the cinnamic alcohol derivatives (monolignols) participating in lignin biosynthesis. By coupling of various radical forms quinone methides are formed, the intermediates of central importance for the formation of lignin polymers and also for the formation of lignin- carbohydrates complexes (LCC) through the covalent bonding with pre- existing polysaccharides in lignification medium. Growth of lignin macromolecule and formation of LCC are taking place through the attacks of various on quinone methide intermediates.

For the biosynthesis of guaiacyl lignin in gymnosperms and guaiacyl- syringyl lignin in angiosperms (except for grasses), only L-phenylalanine is used as substrate. For grass lignins, which contain guaiacyl, syringyl and p- hydroxyphenylpropane units plus p- coumaric acid units esterified to terminal hydroxyl units of propane side chains ( $\beta$  - carbons), both L- phenylalanine and L- tyrosine are used as substrates.

Aspen lignins contain additionally p-hydroxy benzoic acid linked to phenylpropane units through  $\beta$  - carbon of the propane side chain by an ester bond.

Despite the presence of numerous asymmetric carbons in their structures lignins are achiral, which is explained by their formation through the polymerisation of free radical precursors. The major substructure, the arylglycerol -  $\beta$  - aryl ether substructure, comprises about half of the total interunit linkages in both lignin of softwoods and hardwoods of the temperate climatic zone. Lignins are covalently bonded to

polysaccharides of the wood cell walls through the mentioned reactions of quinone methides, through benzyl ester and benzyl ether bonds as the most likely types of bonds occurring in lignin- carbohydrate complexes (LCC).

### **Polyphenols of woody plants other than lignins**

The same "woody" phenolics that are found in a wide range of ferns, gymnosperms, monocotyledons and dicotyledons (in leaves in particular), which means in vascular plants which are lignified are not found in major part of mosses, algae, lichens and fungi. These phenolics are concerned with the development of vascular system in some way in those plants that contain them and therefore they accompany the lignified tissues..

Three types of polyphenols predominate in the leaves of vascular plants :

- Leucoanthocyanidins (proanthocyanidins) -condensed tannins are related to these
- Flavonol glycosides : principal ones being the glycosides of kaempferol (with phenolic B- ring), quercetin (with catechol B- ring) and myricetin (with pyrogallol B- ring). The A-rings of all these flavonols are phloroglucinol ones.
- Esters, glycosides and amides of the various cinnamic acid derivatives (principally p- coumaric, caffeic, ferulic and sinapic- all important for monolignols biosynthesis, therefore all directly related to lignin biosynthesis. One of the most familiar examples of this class of phenolic metabolites is the chlorogenic acid , which is directly related to lignin biosynthesis intermediates: 5-O-caffeoyl ester of quinic acid.

Divergence of biosynthetic routes for lignins and for flavonoid polyphenols consists of:

- Sequential hydroxylation and methoxylation of aromatic rings leading to cinnamic acid derivatives formation which by successive reduction yield cinnamic aldehyde and ultimately cinnamic alcohol derivatives for the biosynthesis of lignins
- Two types of enzymes involved in biosynthesis of flavonoids: general phenylpropanoid biosynthesis enzymes until the formation of cinnamic acid derivative and chalcone synthase, as key enzyme for chalcone intermediate formation by cyclisation reaction between CoA of p-coumaric

acid and malonyl-CoA.

The flavonoids are one of the major groups of polyphenols. Their chemical structure is based on  $C_6C_3C_6$  skeletons, in which the B-ring and carbons 2,3 and 4 in chroman (C-ring) originate from a phenylpropanoid metabolism, i.e. L-phenylalanine and that of ring A from acetate (malonate) metabolism. This was established using standard isotopic tracer methods. The central C15 metabolic intermediate in formation of flavonoids is the chalcone or its isomeric flavanone and the chalcone synthase is therefore the key enzyme for flavonoid biosynthesis. Pathways to the various classes of flavonoids from naringenin (flavanone isomeric to naringenin chalcone with 4',5,7-hydroxylation pattern) involve several enzymes.

### **Vegetable tannins**

Vegetable tannins occupy the borderland of science between botany and chemistry. By mistake, many low molecular mass substances were classified as tannins. The most concise definition of vegetable tannins is that these are water soluble phenolic compounds with molecular mass between 500 and 3000, giving typical phenolic reactions, such as blue coloration with ferric chloride, with special properties such as the ability to precipitate alkaloids, gelatine and other proteins. A typical polyphenol with relative molar mass of 1000 possesses 12-16 phenolic groups and about 5-7 aromatic rings. The capability of precipitating alkaloids, gelatine and other proteins from solution through complexation reactions is of importance for molecular recognition, for possible biological function, but also for a wide range of applications of these plant polyphenols.

There are three types of plant polyphenols which are comply with the definition of vegetable tannins:

- **condensed proanthocyanidins** with flavan-3-ols as fundamental units (catechin nucleus). Condensed proanthocyanidins exist as oligomeric forms (soluble) consisting of 2-5 or six catechin units and polymers which are insoluble. The flavan-3-ols are linked primarily through 4 and 8 positions by C-C bonds. The principal flavan-3ols are procyanidins and prodelpinidins (with pyrocatechol and pyrogallol B-ring hydroxylation patterns, respectively. We presented the propelargonidin condensed proanthocyanidins which has B-rings derived directly from p-coumaric acid.

Oligomeric proanthocyanidins are commonly regarded as responsible for many plant properties attributed to condensed tannins. Condensed proanthocyanidins are subdivided to those that are (i) insoluble in water and usual organic solvents- polymers (ii)



those readily soluble in water and not extractable therefrom by ethyl acetate and (iii) those readily soluble in water and extractable therefrom by ethyl acetate. This third category comprise the tip of the iceberg, as it is now well known that the first two categories predominate over the soluble ones. They are of frequent occurrence in ferns and fruits, as well as in gums and exudates.

- **galloyl and hexahydroxygalloyl esters** and their derivatives are almost invariably found as multiple esters with glucose, otherwise designated as **hydrolysable tannins**
- **phlorotannins** in brown algae

By far the greatest proportions of proanthocyanidins found in plants is invariably in form of higher oligomers and polymers. Proanthocyanidin higher oligomers are built in the same way as the dimers and trimers, by the successive addition of phenolic flavan-3-ol extension units through C-4 to C-8 or C-4 to C-6 interflavan linkages

#### **Biosynthesis of proanthocyanidins oligomers, soluble and insoluble polymers**

Present status of knowledge on biosynthesis of oligomeric proanthocyanidins in plants suggests that it is intimately associated with formation of phenolic flavan-3-ols which first forms a proanthocyanidin dimer by a stereospecific nucleophilic capture at C-4 of the putative quinone methide intermediate in flavan-3-ol biosynthesis (flavan-3-ols are formed from dihydroflavones by loss of a water molecule). The dimer then captures a further quinone methide intermediate (or its protonated carbocation equivalent) from flavan-3-ol biosynthesis to generate a trimer and so progressively by the capture of further quinone methides (or protonated carbocation equivalents) oligomers and finally polymers are formed.

Quinone methides are therefore central intermediates in polymer growth of proanthocyanidins. As in the case of lignins, they can be attacked not only by the phenolic hydroxyls from flavan-3-ols, providing in such a way the growth of proanthocyanidin polymers, but also by hydroxyls originating from sugar residues of polysaccharides of the cell walls. This explains the intimate association of proanthocyanidins with wood cell walls components, which implies that these polymers are not wood extractives in the strict sense. Namely, fraction that is extractable is only a small proportion of total proanthocyanidins present in plant material. Plant materials resulting from repeated extractions with methanol retain invariably greater amounts of material which gives various colour tests for proanthocyanidins. One interpretation of these observations is that these forms of plant

proanthocyanidins are covalently bound to an insoluble polysaccharide matrix within the plant cell, in much the same way as lignins are. Covalent bond to lignins are also to be considered as very likely.

Just as in the case of lignins, the *in vitro* synthesis of proanthocyanidins (which mimics the proposed biosynthetic pathways) provides the soluble products which qualitatively and quantitatively match the procyanidins found in particular plant tissues.

### **Plant polyphenols and humic substances**

Resources rich in lignins and other polyphenols decompose more slowly and contribute much more significantly to recalcitrant soil organic matter (humus) than proteins and sugars, for example. The theory that considers lignin, but also the polymeric polyphenols such as proanthocyanidins, as preserved plant polymers, which are bonded to soil matrix as only partly degraded and chemically modified, can therefore be regarded as the most probable hypothesis when forest residues are considered as starting humus resources. Both degradation and condensation probably occur during humification process. Tentative structural formula for humic acids should probably include more lignin related substructures and inter- units linkages (as lignin is the most abundant polyphenolic polymer), after this hypothesis is verified through the comparative study proposed here.

Conceptually, humic substances can be visualised as combinations of biodegraded biopolymers from plant residues, the lignins being most important because of their abundance in forest residues that are considered here. The structure of the resulting humus will be dependent on the conditions of biodegradation and the combinations of the biodegraded blocks.

Lignin transformation due to biodegradation is characterised by oxidation, side chain and ring cleavage, secondary condensation and hydroxylation. The extent of these transformations is dependent on the initial lignin structure and on the nature of the microbes present in soil. Therefore the initial lignin and other polyphenols structures and environmental conditions are of the decisive importance for the structure of the humic substances formed.

Typical phenylpropane units of lignins  $\square$ -aryl ether ( $\square$ -O-4), diaryl ether, biphenyl, phenylcoumarane and pinoresinol have good chances for survival the process of biodegradation. The amount of methoxyl and phenolic hydroxyl groups depends on the plant source. It can reasonably be assumed that some methoxyl groups are preserved and subsequently demethylated leading to formation

of hydroquinones and finally to o-quinones.

Comparative analysis of the humic substances and their predecessors, in the case of forest humus, lignins and proanthocyanidins, is of primary importance.

Study of plant polyphenols: lignins and polymeric proanthocyanidins in RCW is fundamental for understanding and optimising the transformation of these materials into humus constituents essential for fertility of soils

Polymeric proanthocyanidins are chosen for the study along with lignins as polymers always require a large amount of metabolic energy to be synthesised and because of their already well documented dominance in plant materials present in chipped forest residues that we have designated as RCW. Small branches and twigs consist of high proportions of bark, which is a rich source of polymeric proanthocyanidins (condensed tannins), and juvenile wood which is characterised by lignin quite different from that from the mature wood.

Destructive (wet- chemistry) and non- destructive methods will be applied in such a study, since an important parallelism in methods which are currently applied for the structural studies in lignin and humic substances already exists.

### **Conclusion**

A comparative study of lignins and proanthocyanidins from defined wood species with humic (and fulvic) acids isolated from humus of the related origin is of interest as it could contribute further to better understanding of transformations of lignins (and other polyphenols) leading to major structural fragments of humic acids and their reactivities in soils. Better understanding of humus formation could help optimise the process of RCW application for humus formation and enable its application for upgrading and remediation of arid soils in different regions of the world.

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Wood Chemistry - Lignin Chemistry - Chemistry of Wood Extractives. Structure and reactivity of lignins - fundamental to all chemical pulping technologies, but also to other wood technologies, such as wood preservation. Better utilization of lignins as by-products of pulping industry - better environmental protection and value- added products. Study of the nature of chemical linkages between lignins and polysaccharides in lignin-carbohydrate complexes (LCCs) of different types of woods and pulp. Implications of lignins and LCCs for humus formation. Study of wood and bark polyphenols biosynthetically related to lignins.. polymeric proanthocyanidins are of special interest. Forest products such as essential oils and resins and extractives in broader sense are another field of my research interest. The terpene constituents of volatile oils and their importance for chemotaxonomic relations is another research project I am involved in. The most recent one is related to triterpenoid constituents of birch barks.

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## Recent Industrial Applications of Lignin: A Sustainable Alternative to Nonrenewable Materials

Jairo H. Lora<sup>1</sup> and Wolfgang G. Glasser<sup>2,3</sup>

Lignin represents a vastly under-utilized natural polymer co-generated during papermaking and biomass fractionation. Different types of lignin exist, and these differ with regard to isolation protocol and plant resource (i.e., wood type or agricultural harvesting residue). The incorporation of lignin into polymeric systems has been demonstrated, and this depends on solubility and reactivity characteristics. Several industrial utilization examples are presented for sulfur-free, water-insoluble lignins. These include materials for automotive brakes, wood panel products, biodispersants, polyurethane foams, and epoxy resins for printed circuit boards.

**KEY WORDS:** Lignin; biopolymers; adhesives; biodispersants; OSR; polyurethane foams; epoxy resins; wood; pulp and paper.

### INTRODUCTION

Lignin is nature's most abundant aromatic (phenolic) polymer. Its principle function is to provide trees with the ability to raise a crown above ground level [1, 2]. Lignin is separated from wood during pulp and papermaking operations, where it serves primarily as fuel. Only a small amount (ca. 1–2%) is isolated from spent pulping liquors and employed in a wide range of specialty products. These, however, amount to 1 million tons per year worldwide [3, 4].

### TYPES OF LIGNINS AND THEIR PROPERTIES

Lignins vary in structure according to their method of isolation and their plant source [2, 5–7]. Hardwoods develop a different lignin than softwoods, and annual

crops are different again. However, the differences are minor as far as most applications are concerned. Major differences exist between lignins derived from different pulping processes. The traditional sulfite process generates a water-soluble polymeric derivative in admixture with degraded carbohydrates. An aliphatic sulfonic acid ( $\text{SO}_3\text{H}$ ) function becomes part of the lignin backbone ensuring ready water-solubility in the presence of a suitable counter ion (Na, Ca, Mg,  $\text{NH}_4$ , etc.). "Kraft" or "thio" lignins are generated during kraft pulping in alkaline medium. They contain a small number of aliphatic thiol groups that give the isolated product a characteristic odor, especially during heat-treatment. A very small amount of kraft lignin is isolated from pulping liquors in the United States and Europe [4]; the vast majority is used as in-house fuel required for the recovery of chemicals. Kraft lignins are dark-colored and water- and solvent-insoluble products that dissolve in alkali owing to their high concentration of phenolic hydroxy groups. Neither lignin sulfonates nor kraft lignins undergo a distinctive glass-to-rubber (or fluid) transition when heated, despite the fact that lignin in wood has a  $T_g$  of under  $100^\circ\text{C}$  [8]. Numerous other lignin products and derivatives have been

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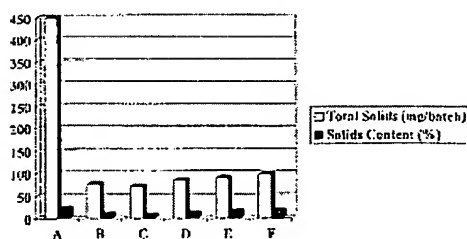


Fig. 3. Biocidal activity of various white water sludge formulations. (Data based on treatment of 5-L batches of white water containing 4.6 g/L total solids of which 65% were  $\text{CaCO}_3$ . The bars represent (A) control (blank); (B) soda straw lignin; (C) soda flax lignin; (D) a commercial lignin sulfonate solution as used conventionally for sludge control; (E) a commercial biocide solution containing methylene-bis-thiocyanate; and (F) a commercial biocide solution containing a quaternary ammonium salt [50].

as in paper machine recirculating ("white") waters [50]. Slime deposition in the white water of paper machines is generally prevented by the addition of biocides of different origin. Both total amount of slime (in dry matter per liquid volume) and slime solids content (in percent) are critical parameters. The latter relates to the ease of resuspension of deposited slime via the shear forces of the circulating fluid when the turbulence of the flow is adjusted.

Published data obtained with industrial white water samples (5-L batches) treated with different biocidal mixtures revealed high effectiveness of nonwood soda lignins (Fig. 3). The product is currently used in several paper machines in Europe, where it is displacing more toxic, less-environmentally friendly products. The product is dosed at the level of 100–200 ppm (based on weight of paper produced) at a location of the water circuit where good agitation and mixing are promoted.

## CONCLUSION

New applications are emerging for specialty, sulfur-free lignins in diverse areas, principally as sustainable alternatives to nonrenewable products, such as phenolic and epoxy resins, and isocyanates. This is in addition to industrial efforts that aim at using lignin as the principal component of thermoplastic materials [51]. The latter represents an activity for which little published information exists so far. The ability for lignin to make significant impact in these areas, however, depends on its availability in industrial quantities as a high-purity product, preferably in a sulfur-free form.

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